



**The Development and
Performance Testing of
Adsorbent Carbon for the
Storage of Compressed
Natural Gas**

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Energy
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Program



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Energy

The Development and Performance Testing of Adsorbent Carbon for the Storage of Compressed Natural Gas

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Abstract: Work has continued in a long-term program to develop adsorbent carbons for storing compressed natural gas at low pressure on board vehicles. Some promising composite carbons made of mixtures of polyvinylidene chloride (Saran) and commercial charcoals have been prepared in monolithic form in litre quantities. Those have been subjected to repeated fill-empty cycling with a commercial-grade gas to measure the effect of impurities on the amount of gas delivered. Work has also proceeded to improve the formulation by preparing gram samples of various proportions of Saran and charcoals. These have been tested for basic adsorption properties, and promising compositions have been selected for scaled-up fill-empty cycling. Finally, attempts were made to improve the basic adsorption properties of Saran-derived carbons by incorporating fluorine atoms into the material. No positive benefits were found in this case.			
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EXECUTIVE SUMMARY

The work described in this report is part of a long-term program to develop carbon adsorbents for storing natural gas on board vehicles. It has been directed by the Ontario Ministry of Transportation and Communications and funded by the Ontario Ministry of Energy.

Extensive fill-empty cycling of kilogram-sized samples of Saran and Saran composite discs has been carried out with commercial-grade natural gas. Results show that the volume of gas delivered decreases by about 10% after a few cycles but then remains virtually constant over 50 to 100 further cycles. The amount of gas delivered depends on the carbon composition. A particular 50/50 Saran/Amoco composite was found to deliver more gas than pure Saran carbon; more than 100 volumes of natural gas can be repeatedly delivered from a unit volume of storage at 3.5 MPa (500 psi).

Work has continued also with smaller gram-sized samples to identify materials with improved performance. Physical properties and adsorption of methane at pressures up to 7 MPa (1000 psi) at 25°C have been determined. Indications are that new formulations, when prepared in kilogram-sized quantities and cycled, will deliver more gas than the 50/50 composite already reported.

Work will continue in the search for improved and cheaper materials and in ways of delivering more gas from adsorbents, e.g., by heat input.

1/ INTRODUCTION

At present, natural gas as a vehicular fuel is stored exclusively as compressed gas in heavy-walled steel cylinders at pressures from 13.8 to 20.7 MPa (2000 to 3000 psi). An attractive alternative to this would be the storage of a similar quantity of gas in the same volume at lower pressures, e.g., 3.5 MPa (500 psi), by employing an adsorbent in the storage system.

Methane, when compressed at 13.8 MPa (2000 psi), has a density of 108 g/L. To be acceptable, an adsorbent system should have a similar capacity. In several investigations [1-3] using commercially available adsorbents and pressures less than 3.4 MPa (500 psi), this storage density has not been achieved. This is, in part, due to inefficient use of the available space because of poor packing of the adsorbent, resulting in large inter-particle voids [4], and to the relatively lower proportion found in commercial carbons of the finer pores more suitable for methane adsorption [5]. The inter-particle voids can be reduced by compressing [2], grinding, and sieving [6], or by producing a specially shaped adsorbent to efficiently fill the storage vessel [4]. By using this latter technique, employing Saran carbon disks which have a very fine pore structure, it was possible to store more methane per unit volume at 3.4 MPa (500 psi) than had previously been reported, 99 g methane/L (149 scf/ft³).

The present investigation had three main objectives:

- 1/ the production of composite carbons by binding a commercial carbon with a polymer, followed by pyrolysis, in an attempt to improve the adsorption of methane per unit volume;
- 2/ the activation of microporous carbons by introducing fluorine molecules into the pores in an effort to provide a more polar and, consequently, more attractive site for methane adsorption.
- 3/ to study the effect of repeated fill-empty cycling using natural gas in place of methane on Saran carbon disks under different pressures and fill-empty cycle times.

2/ COMPOSITE CARBON ADSORBENTS FOR NATURAL GAS

2.1/ Introduction

It was previously shown [4] that to be successful in maximizing methane or natural gas adsorption per unit volume at ambient temperatures, adsorbent void and macropore volume must be minimized and micropore volume, maximized. The larger the micropore volume per unit storage volume, the greater the amount of methane or natural gas stored.

It is conventional to express activity as surface area, which is closely related to micropore volume for highly adsorbent carbons. Therefore, for simplicity, surface area will be used as the critical parameter in assessing potential methane adsorbency.

Amoco-type carbons have very high surface areas per gram (2500 to 3000 m²/g). On a mass basis, they adsorb more methane than any other carbon, but they have very low packing densities (0.30 g/mL). This is because they have a large void and macropore volume. Their surface area per unit volume is, therefore, relatively small (900 m²/mL).

If the inter-particle void space could be removed, the packing density of the Amoco-type carbon would be 0.45 g/mL. The surface area per millilitre would then be 1350 m²/mL. Saran carbon has an area of 1100 m²/mL. This suggests that Amoco could, if void space is eliminated, adsorb more methane than Saran carbon, from a volume consideration.

Compaction by compression of Amoco-type carbons is possible, but on removal of the compressive force on the carbon, it returns to its original apparent or packing density and shows little or no agglomeration. This may be due to gas adsorbed on its surface. If, however, some Saran polymer is added, the Amoco carbon, after compression, remains compacted. Subsequent carbonization of the bonding polymer yields a composite carbon with a density reflecting the composition of the original mixture. There are significant advantages in doing this to improve the volume utilization of a storage vessel.

Materials were made as described in Section 2.1.1, and some of their properties are listed in Tables 1 to 6. Figure 1 shows the theoretical bulk density versus composition curve for Saran/Amoco carbon composites, calculated from the known bulk densities of each carbon. A composite of known composition having a density below this curve must contain some of the original inter-particle voids. A composite density above the curve suggests that voids have been eliminated and that Saran carbon now occupies some macropore volume of the Amoco carbon, the polymer having

entered during the mixing stage. Such a high-density composite should show more methane adsorption per unit volume.

Another theoretical curve for Saran/Amoco carbon composites can be made for surface area or micropore volume. Figure 2 shows the relationship between composition and surface area per unit volume, assuming zero inter-particle void and no macropore penetration, i.e., the composite has a density on the theoretical curve in Figure 1.

From Figure 2 it is apparent that, for any composition, a composite has the potential to have a surface area greater than $1100 \text{ m}^2/\text{mL}$, even if some inter-particle void remains. In reality, this may not be the case, if, in the production of the composite, some micropores are destroyed or blocked off. It may also be impossible to produce coherently shaped composites with high-percentage Amoco content.

It is possible to take this same theoretical approach with other commercially available carbons such as Calgon BPL or AC Carbone CNS. These carbons do not show as much potential for greater methane adsorption because of their lower surface area. From a practical standpoint, however, they merit some consideration, since they are cheaper and their composites with Saran carbon can be made relatively easily.

Composites with Saran, to date, have been made by mixing a carbon with Saran polymer and compressing it in a hydraulic press. By heating the die to melt the polymer, a higher density disk could be produced than by cold pressing. It was hoped that by doing this, not only were the inter-particle voids being eliminated but that some polymer would enter the macropore system of the carbon. This technique was only partly successful.

Another approach was taken using Saran 159 (Dow Chemical Co.), a latex. By an optical scattering technique, the average particle size in the latex was measured as 147 nm diameter. This figure is smaller than the average macropore diameter of the Amoco-type carbon, AX-21 (Anderson Development Co.), and it was hoped, since AX-21 has up to 1.4 mL/g macropore, that some of this volume could be occupied by the latex particles and so produce a higher density composite carbon. A similar method of macropore filling by soaking the carbon in a tetrahydrofuran solution of the polymer was also undertaken. Following this general approach, it should be possible to produce an adsorbent capable of storing more methane per unit volume than any reported to date.

2.1.1/ Experimental

A series of homogeneous mixtures of Saran 159 latex and Anderson AX-21 carbon was prepared, with polymer content ranging from 20 to 80% by weight. These samples were dried and pressed into 1.5 cm diameter pellets or disks in a heated die. The temperature of the die was kept low enough to prevent degradation of the polymer, which would result in blistering or bubbling and the creation of unwanted macropores. Mixtures containing less than 30% polymer did not agglomerate.

The pressed pellets were then slowly pyrolyzed in a vacuum to 700°C, at which point the polymer was completely carbonized. The resulting composite carbons had percentages of AX-21 carbon ranging from 50 to 90% by weight. All of these composites remained as coherent pieces, but those with higher percentages of AX-21 were somewhat friable and had low densities, as calculated using the geometric volume, determined by measurement of a regularly shaped piece.

Low-temperature (77 K) nitrogen isotherm measurements were used to measure the BET [4] surface area and micropore volume of all the samples, and high-pressure mercury porosimeter measurements, to find the macropore volume and density. Methane adsorption isotherms at 25°C and pressures to 7 MPa (1000 psi) were measured for all the samples.

Saran 506 (Dow Chemical Co) is a copolymer of 85% polyvinylidene chloride (PVDC) and 15% polyvinyl chloride (PVC). Another series of composite carbons was prepared using Saran 506 dissolved in tetrahydrofuran. Varying amounts of dried AX-21 carbon were added to polymer solutions and then evaporated to dryness with constant mechanical stirring. The dried mixture was pressed into pellets and pyrolyzed in the same way as before. The composite carbon pellets had maintained their shape and were hard and durable. The abbreviation THF is used in the tables to identify composites made by this method. This series was characterized and the methane adsorption measured using the same methods as for the Saran 159 series.

2.1.2/ Discussion

In Figure 1, the densities from the measured geometric volume of the carbon composite pellets are plotted with the theoretical bulk density curve. At high AX-21 composition, such as the 90 and 86% by weight pellets, the densities are lower than the theoretical curve, indicating the existence of inter-particle voids. For the composites with less than 80% by weight AX-21 composition, the densities are above the theoretical curve, suggesting that penetration of the polymer latex particles into the macropores of the AX-21 carbon had taken place.

Another indication of this penetration into the macropores can be seen in Figure 3, which shows the mercury porosimetry plots of the carbon from latex composites. In Table 1, the total macropore volume, calculated from these plots, is seen to decrease with decreasing AX-21 composition. The most interesting evidence from these plots is the reduction in the mercury intrusion volume in the 1 to 2 μ m diameter region ($\text{LnP} = 4.4$), where any excess volume is really void space, useless for methane adsorption.

Table 1 also lists the BET surface areas per gram of composite and the areas per millilitre calculated using the geometric density of the composite. A slight increase occurs relative to the 1100 m^2/mL value for 100% Saran carbon. This is also evidence for filling of the macropores.

All of this evidence suggests that better use is being made of the available volume by this method of producing composites.

For the composite carbon pellets produced by the Saran 506/tetrahydrofuran solution method, the densities after pyrolysis, shown in Table 2, are quite high. This seemed to be an encouraging improvement, but along with this increase in density there was a decrease in surface area. The area per millilitre of carbon had not increased and was actually lower than the 100% Saran carbon value. This is difficult to explain, but a blocking of the micropores must be considered. This blocking could occur if the solvent allowed the polymer to enter into the meso or micropores of the AX-21 carbon.

The mercury porosimeter plots are shown in Figure 4. From these it is evident that the 48% AX-21 composite has little macropore volume. Although the pore volume is minimized in the 1 to 2 μ m diameter region ($\text{LnP} = 4.4$), it has also been reduced in the smaller diameter pore region from 9 down to 3 nm diameter ($\text{LnP} = 9.9$). This is close to the critical microporous (and adsorbent) region.

For the 63 and 68% AX-21 composites produced by this method, the larger, 1 to 2 μ m diameter, region has not been filled, while the 9 to 3 nm region is greatly reduced in volume, indicating that the polymer has penetrated into or blocked the entrance to this region which contributes to the total micropore volume.

Figure 5 compares the mercury porosimetry plots of two composites having the same composition but prepared by distinctly different methods. One is prepared from the Saran 159 latex, while the other is made from Saran 506 using tetrahydrofuran as a solvent. Both have 63% AX-21 carbon by weight, but the macropore volumes, shown in Figure 6, vary greatly, as do

the pore volume distributions. This discussion clearly shows how the macropore volume of a composite can be altered by the method of preparation.

In an attempt to open the "blocked" micropores in the 68% AX-21 composite, prepared from the tetrahydrofuran solution, a short steam activation was carried out at 850°C. After only 1 h of activation, the sample lost 47% of its weight. The surface area was increased to 2200 m²/g from 1680 m²/g. However, the macropore volume had increased to 2.4 mL/g, and the density was reduced to a very low 0.30 g/mL. The product, as might be expected, was very friable.

Methane adsorption isotherms at 25°C are shown in Figure 7 for the Saran 159 series of composites. The amount of methane adsorbed per gram increased with increasing AX-21 content. This trend is reversed, as shown in Figure 8, where the adsorption per millilitre of composite is plotted. Values for this latter plot were calculated using the geometric densities of the pellets.

The composites with 63 and 73% AX-21 by weight, which are mechanically strong, show such increased adsorption on a volume basis, that a larger sample should be made for cyclic testing. The amounts of methane adsorbed at 25°C by these composites for some specific pressures are listed in Table 3, on both a mass and a volume basis. From this table, the important part that density and composition play on the amount of methane stored per unit volume is clearly apparent.

Figures 9 and 10 show the methane adsorption of composites produced by the tetrahydrofuran solution method. Table 4 gives the methane adsorption at 25°C for the composites made by this method. Perhaps, as expected from the characterization of these composites, this method results in samples which are poorer adsorbents for methane.

To get some idea of the efficiency to which the methane is stored in the micropore of the Saran 159 latex-based composites, in Table 5, the saturation density of methane at 25°C is given, along with the methane storage density at various pressures. The ratio of these is the degree of saturation. This figure turns out to be remarkably constant for all the composites at any of the given pressures.

This constancy suggests that the micropore system of any one composite is equally attractive as another to methane molecules. If this is the case, the composites with the greater micropore volume per unit packing volume will show greater methane adsorption per unit volume. Again, the

composites with 63 and 73% AX-21 are identified as being better in this regard.

As a comparison, the methane adsorption at 25°C for the 80% AC Carbone/20% Saran carbon and the 50% AX-21/50% Saran carbon composites used in the cyclic testing part of this report has been listed in Table 4. When their values are compared to the Saran 159 latex series in Table 3, it is apparent that, based on the small samples, there is a potential for an increase in storage capacity using composites made from this latex.

Using the values from Tables 3 and 4, it is possible to carry out a theoretical extrapolation and predict the amount of methane which might be delivered from a storage vessel containing these composites. The results are listed in Table 6. The assumption is made that there is no void space in the vessel and that equilibrium (maximum) adsorption has taken place, and so these values are likely to be optimistic. However, in the cyclic testing, described in Section 4, it has been found that slightly higher values are obtained experimentally than predicted. These experimental values, of course, include the amount of gas stored as compressed gas in the void and macropore. These amounts are not considered in the predicted delivery calculation used to obtain the values given in Table 6. Thus, although a percentage value is difficult to put on any increase in storage capacity, there is sufficient evidence to suggest there will be one and that this should be verified experimentally.

2.1.3/ Summary on Composite Carbons

Composite carbons, made from a mixture of Anderson AX-21 and Saran carbon, are potentially good adsorbents for methane from a volume consideration.

Two series of varying percentages of these composites were made. Their method of preparation was distinctly different, and the resulting composites have quite different properties. Those made from Saran 159 latex were better adsorbents of methane per unit volume than those made from Saran 506 tetrahydrofuran solution.

From measured isotherms on small samples, two composite carbons were identified as being good prospects for delivering more methane per unit volume than has currently been achieved. These products should be investigated further on a larger scale.

3/ FLUORINE ACTIVATION

It has been suggested that the adsorption of methane at ambient temperatures may be increased by providing a more polar surface. Fluorine, the most polar element, was chosen because it chemisorbs onto carbon and is not desorbed from the surface when methane is desorbed. Because fluorine is such a violently reactive and toxic substance, the considerable experimental difficulties in using it had to be overcome. For example, it reacts with any grease, rubber, or oil in a system. Any glass or steel has to be passified before it can be used.

Fluorine reacts with carbon at temperatures of 250 to 400°C to various degrees, depending on the graphitic nature of the carbon. Although a McBain Bakr balance was used to follow the weight change, it was not possible to establish how much fluorine was on the carbon surface. This was because the fluorine reacted with some of the carbon to produce a volatile polymeric material of indeterminate composition, which condensed on the walls of the cooler part of the system as a white solid. Thus, in the initial stages of fluorination, a net weight loss was observed, even though visibly the nature of the carbon surface had changed to a chocolate brown colour.

Fluorination was carried out on Saran carbon and on AX-21 Amoco-type carbon to varying degrees. The fluorinated carbons thus produced were then characterized as to surface area and micropore volume from a -196°C nitrogen isotherm. They were then investigated for methane uptake at 25°C.

Every sample produced showed a substantial reduction in surface area and micropore volume and adsorbed considerably less methane than the original carbon. These results were disappointing, especially so when the time and effort to carry out these experiments is considered. Further fluorination of carbons would not seem to be a worthwhile venture.

4/ FILL-EMPTY CYCLING USING NATURAL GAS

4.1/ Introduction

A few years ago the Ford Motor Company conducted some interesting work investigating both zeolites and carbons as possible adsorbents for natural gas [6,7,8,9]. In these studies they identified the important parameters which contribute to and detract from increased methane storage density. They also carried out a fill-empty cycle test for 100 cycles on Union Carbide 9LXC carbon which had been ground and sieved to increase its packing density. Natural gas at 21°C and pressures to 12 MPa (1700 psi) was used. Fill-empty times were indeterminate because equilibrium values were used. Over the course of this cycling test, a decrease of some 20% in the storage capacity was observed, but this decrease was non-linear and predicted not to exceed 25% over 1000 cycles.

In a previous report [4], where methane was used on Saran carbon disks, there were no higher hydrocarbons present and so no significant decrease in storage capacity was observed.

4.2/ Experimental

The apparatus used was the same one as described in the last report [4]. The solenoid valves were replaced by Asco 8262C200 valves, suitable for pressures to 10.3 MPa (1500 psi). Natural gas, obtained from a local CNG vehicle filling station in Kingston, was used instead of methane.

In an attempt to simulate real life scenarios, two different filling times were used:

- 1/ a quick-fill of 15 min
- 2/ a 4 h fill, representing the overnight fill

Both were emptied to 0.007 MPa (1 psig) over a 2 h period. The first cycle of the quick fill was, in fact, a slow fill (4 h). This was done to establish an "equilibrium" storage capacity and to verify that degassing of the carbon from a previous run had successfully removed any higher hydrocarbon buildup.

Three types of carbon were used in the same disk-shaped packing format described previously. One was the same Saran carbon as used for the methane cycling [4]. The other two were composite carbons, which combined 50% Saran carbon with Anderson AX-21, and 20% Saran carbon with AC Carbone CNS-196, an activated coconut carbon, respectively. Their properties are given in Table 7.

Repeated fill-empty cycling was carried out at three pressures, 2.1 MPa (300 psi), 3.4 MPa (500 psi), and 6.9 MPa (1000 psi). The number of cycles conducted at different fill times and pressures varied from 20 to 280 and are given in Table 8.

To investigate the effect of heating on desorption, a heater tape was placed around the outside of the storage vessel. After filling for 15 min, the heater was switched on for 30 min before emptying began. It was switched off midway during the emptying period of 2 h. The maximum temperature in the vessel was controlled to either 150 or 250°C.

4.3/ Results

The result of each cycle test has been presented graphically in Figures 11 to 23, giving the amount of natural gas stored in the vessel after filling and the amount of gas remaining after emptying. The difference between these is the amount delivered for each cycle, which is also shown. This value has been plotted separately for a quick fill and a slow fill situation for several carbons and filling pressures; these are shown in Figures 24 to 28.

The fuel delivery is presented another way in Figures 29 to 31, which show the effects of pressure for some selected fill rates and carbons. Finally, the amount delivered by the two best carbons at 3.4 MPa (500 psi) is compared in Figure 32 for a 15 min fill time and in Figure 33 for a 4 h fill time.

The results are tabulated in Tables 9 and 10, where the amounts stored and delivered, respectively, are indicated under various cycling conditions.

4.4/ Discussion of Cycle Testing

Over 4000 h of cyclic testing have been carried out using natural gas. The 100% Saran carbon disks have been subjected to more than 700 fill-empty cycles. After this time, to see if there was any detectable deterioration in their performance, they were degassed under vacuum at 200°C and then cycled under the same conditions as when cycling was first started. They had the same adsorbent capacity, and their physical properties were unchanged.

The buildup of higher hydrocarbons reported by the Ford cyclic test on 9LXC carbon was also observed for all three carbons under all conditions.

Mass spectroscopic analysis of this adsorbed material was carried out using a VG Micromass Q4 by slowly warming the carbon under vacuum. It was found to be mainly ethane, with lesser amounts of water, carbon dioxide, propane, and butane.

The results for nearly all the tests show that this buildup causes an initial decrease in the amount of natural gas delivered, but after some 40 or so cycles, the amount delivered remains virtually constant (even after 280 cycles in one case). The decrease in the deliverable amount of natural gas is, in general, about 10%. This should be considered tolerable for adsorbent storage systems. The buildup can be removed and the carbon restored to its maximum adsorptive capacity by heating to 200 to 250°C.

Although the heat of adsorption caused a temperature rise to as much as 70°C, the 4 h time period for the slow fill was sufficient to allow the vessel to return to ambient temperature before filling stopped and emptying began. However, this was not the case for the 15 min fill, where filling stopped when the vessel was still some 30°C above ambient. The quick fill, therefore, suffers in two ways -- the short time period for adsorption and the higher temperature of the adsorbent -- both of which contribute considerably to a reduction in storage capacity.

During the 2 h emptying period, the temperature dropped more than 20° below ambient initially but, by the end of this time, had virtually returned to ambient temperature again.

Differences in temperature profile during cycling were noted for the different carbons but were not considered great enough to be significant.

Because of the buildup of adsorbates on the carbon, it is not easy to define the amount of gas stored in the vessel, nor is it of much value unless heating were to be employed to remove it. Of much greater use is the amount of gas which can be delivered from the vessel with each cycle. The results obtained are very significant. While the 100% Saran carbon disks are better from an overall storage capacity viewpoint, the composite of 50% Saran and 50% AX-21, even though it stores less, delivers between 15 and 20% more natural gas when filled at 3.4 MPa (500 psi). When filled at 2.1 MPa (300 psi), it delivered about the same as the 100% Saran carbon. About 69.0 g/L (104 scf/ft³) was consistently delivered after a 4 h fill at 3.4 MPa (500 psi). It was about 10% less using a 15 min fill. Compressed natural gas at 13.8 MPa (2000 psi) delivers 107 g/L (160 scf/ft³). Thus, at one-quarter of this pressure, an adsorption system can deliver two-thirds of this amount.

The amount of gas which is not desorbed during the emptying cycle is substantial. Depending on the fill pressure, it can appear to be as much as the amount delivered or 50% of the amount stored in the vessel. In fact, it is less, due to the buildup which has taken place. With no buildup, it would still be some 30%, or one-third, of the storage capacity. This is too large an amount to be acceptable.

A simple way to reduce this and deliver more gas during each cycle is to heat the adsorbent. In doing this, however, the adsorbent remains hot when filling is begun on the next cycle, the consequence of which is less natural gas is stored. At 2.1 MPa (300 psi) only 35 g/L of natural gas were both stored and delivered at 250°C. This technique is obviously unsatisfactory, but because of the potential improvements to the amount delivered by heating some further investigation is necessary.

4.5/ Summary of Cycle Testing

- The carbons tested showed no change in their physical properties after hundreds of cycles at differing pressures and temperatures.
- Buildup on the carbons from compounds other than methane in natural gas did not appear to be a major problem. The rate of buildup was extremely slow after 30 or 40 cycles. This buildup could be removed by heating the carbon.
- The heat of adsorption did not reduce adsorption capacity when a prolonged filling time was used but did reduce the amount stored in the vessel when rapid filling was carried out.
- For the storage vessel used, enough heat was obtained from the surroundings to overcome the heat of desorption and return the carbon to ambient temperature during the 2 h emptying period.
- The amount of gas not desorbed during emptying is too large to be ignored.
- Of the three carbons used in cyclic testing, the composite of 50% Saran/50% AX-21 carbon delivered as much natural gas and 20% more under some conditions than 100% Saran carbon. However, the Saran carbon stored more than this composite, so if heating were used to remove residual gas, 100% Saran carbon has the potential to deliver more.
- This cycling test apparatus, with a 1 L storage vessel, run automatically by a cheap, simple VIC 20 computer, has been a very reliable and valuable tool in evaluating the performance of an adsorbent. It has

clearly demonstrated that at 3.4 MPa (500 psi), it is possible to store at least 95 g/L (140 scf/ft³) and to deliver 69 g/L (104 scf/ft³) repeatedly from an adsorbent storage system.

5/ REFERENCES

- [1] Barton, S.S., Dacey, J.R., Evans, M.J.B., and Quinn, D.F., "Experimental Evaluation of Selected Adsorption Media for Storage of Compressed Natural Gas," Ontario Ministry of Transportation and Communications, AF-84-01, April 1984.
- [2] Remick, R.J., Elkins, R.H., Camara, E.H., and Bulicz, T., "Advanced On-board Storage Concepts for Natural Gas Fueled Automotive Vehicles," US Department of Energy and NASA, Report 0327-1, June 1984.
- [3] Innes, R.A., Lutinski, F.E., Occelli, M.L., and Kennedy, J.V., "Low Pressure Storage of Methane on Interlayered Clays for Potential Vehicular Application," US Department of Energy, Report CE 50071, July 1984.
- [4] Barton, S.S., Holland, J.A., and Quinn, D.F., "The Development of Adsorbent Carbon for the Storage of Compressed Natural Gas," Ontario Ministry of Transportation and Communications, AF-85-01, May 1985.
- [5] Barton, S.S., Dacey, J.R., Evans, M.J.B., Holland, J.A., and Quinn, D.F., "The Production and Evaluation of Composite Carbons for the Adsorption of Methane," Ontario Ministry of Transportation and Communications, AF-84-04, June 1984.
- [6] Golovoy, A., "Sorbent Containing Storage Systems for Natural Gas Powered Vehicles," SAE Conference Proceedings, 1983, pp. 39, 129.
- [7] Otto, K., "Adsorption of Methane on Active Carbons and Zeolites," Alternative Energy Sources IV, Ann Arbor Science, 1982, p. 241.
- [8] Braslaw, J., Nasea, J., Jr., and Golovoy, A., "Low Pressure Methane Storage System for Vehicles -- Preliminary Concept Evaluation," Alternative Energy Sources IV, Ann Arbor Science, 1982, p. 261.
- [9] Golovoy, A., and Blais, E.J., "Alternative Fuels for Spark Ignition Engines," SAE, Report SP-559, 1983, p. 47.

Table 1/ Properties of Composite Carbons from Saran 159 Latex

AX-21/Saran Carbon Ratio						
	90/10	86/14	80/20	73/27	63/37	50/50
77 K Nitrogen Isotherm						
BET Surface Areas						
m ² /g	2644	2460	2352	2097	1861	1682
m ² /mL	1005	1132	1176	1132	1191	-
Dubinin Micropore Volume						
mL/g	1.20	1.13	1.06	0.97	0.84	0.74
DENSITIES						
Bulk						
g/mL	0.38	0.46	0.50	0.54	0.64	-
HG 1 atm						
g/mL	0.39	0.46	0.52	0.61	0.70	-
HG 414 MPa						
g/mL	0.97	0.92	0.92	1.00	0.99	-
Macropore Volume						
mL/g	1.53	1.08	0.82	0.64	0.41	-

Table 2/ Properties of Other Composite Carbons

	AX-21/Saran Carbon Ratio					AC Carbone/* Saran Carbon Ratio
	From 506 Polymer (THF)		Steam Acti- vated	From 415 Polymer		
	68/32	63/37	48/52	68/32	50/50*	
77K Nitrogen Isotherm						
BET Surface Areas						
m ² /g	1681	1526	1285	2204	1600	907
m ² /mL	1042	931	1002	661	896	664
Dubinin Micropore Volume						
mL/g	0.77	0.69	0.58	0.95	0.69	0.38
DENSITIES						
Bulk						
g/mL	0.62	0.59	0.78	-	0.56	0.71
HG 1 atm						
g/mL	0.58	0.61	0.81	0.30	0.62	0.74
HG 414 MPa						
g/mL	0.98	1.02	0.99	1.14	0.93	1.17
Macropore Volume						
mL/g	0.69	0.66	0.22	2.41	0.54	0.55

*Samples used in cycling tests; large disks pressed cold.

Table 3/ Methane Adsorption of Composite Carbons from Saran 159 Latex,
25°C

		AX-21/Saran Carbon Ratio					
		90/10	86/14	80/20	73/27	63/37	50/50
Methane Adsorbed g/g Carbon							
At 0.1 MPa (15 psi)	0.0187	0.0189	0.0194	0.0189	0.0192	0.0198	
At 2.1 MPa (300 psi)	0.1483	0.1352	0.1273	0.1249	0.1157	0.1038	
At 3.4 MPa (500 psi)	0.1812	0.1648	0.1554	0.1535	0.1403	0.1216	
At 6.9 MPa (1000 psi)	0.2151	0.2057	0.1950	-	0.1775	0.1663	
Methane Adsorbed g/mL Carbon							
At 0.1 MPa (15 psi)	0.0071	0.0087	0.0097	0.0102	0.0123	-	
At 2.1 MPa (300 psi)	0.0564	0.0622	0.0636	0.0674	0.0740	-	
At 3.4 MPa (500 psi)	0.0688	0.0758	0.0777	0.0829	0.0898	-	
At 6.9 MPa (1000 psi)	0.0817	0.0946	0.0990	-	0.1136	-	

Table 4/ Methane Adsorption of Other Composite Carbons, 25°C

AX-21/Saran Carbon Ratio					AC Carbon/* Saran Carbon Ratio
	From 506 Polymer (THF)	From 506 Polymer (THF)	Steam Acti- vated	From 415 Polymer	
	68/32	48/52	68/32	50/50*	
Methane Adsorbed g/g Carbon					
At 0.1 MPa (15 psi)	0.0168	0.0201	0.0171	0.0144	0.0150
At 2.1 MPa (300 psi)	0.0980	0.0872	0.1233	0.0940	0.0678
At 3.4 MPa (500 psi)	0.1168	0.0997	0.1510	0.1134	0.0781
At 6.9 MPa (1000 psi)	0.1358	0.1190	-	0.1395	0.0900
Methane Adsorbed g/mL Carbon					
At 0.1 MPa (15 psi)	0.0104	0.0157	0.0051	0.0081	0.0106
At 2.1 MPa (300 psi)	0.0608	0.0680	0.0370	0.0526	0.0481
At 3.4 MPa (500 psi)	0.0724	0.0778	0.0453	0.0635	0.0554
At 6.9 MPa (1000 psi)	0.0842	0.0928	-	0.0781	0.0639

*Large disks used in cycling tests

**Table 5/ Methane Micropore Densities for Composite Carbons from Saran
159 Latex**

	AX-21/Saran Carbon Ratio					
	90/10	86/14	80/20	73/27	63/37	50/50
Dubinin Saturation Density g Methane/mL Micropore	0.248	0.239	0.238	0.255	0.275	0.296
Methane Adsorbed g/mL Micropore						
At 2.1 MPa (300 psia)	0.124	0.120	0.120	0.129	0.138	0.140
At 3.4 MPa (500 psia)	0.151	0.146	0.146	0.158	0.167	0.164
At 6.9 MPa (1000 psia)	0.179	0.182	0.183	-	0.211	0.225
Degree of Saturation						
At 2.1 MPa (300 psia)	0.500	0.502	0.504	0.506	0.502	0.473
At 3.4 MPa (500 psia)	0.609	0.611	0.613	0.620	0.607	0.554
At 6.9 MPa (1000 psia)	0.722	0.762	0.769	-	0.767	0.760

Table 6/ Predicted Delivery (g/L) from Methane Adsorption Isotherms,
25°C

Carbon	Pressure		
	2.1 MPa	3.4 MPa	6.9 MPa
90/10 AX-21/Saran from 159 Latex	49.3	61.7	74.6
86/14 AX-21/Saran from 159 Latex	53.5	67.1	85.9
80/20 AX-21/Saran from 159 Latex	53.9	68.0	89.3
73/27 AX-21/Saran from 159 Latex	57.2	72.7	-
63/37 AX-21/Saran from 159 Latex	61.7	77.5	101.3
68/32 AX-21/Saran from 506 Polymer (THF)	50.4	62.0	73.8
48/52 AX-21/Saran from 506 Polymer (THF)	52.3	62.1	77.1
68/32 AX-21/Saran 47.0% Burn-Off Steam Activation	31.9	40.2	-
50/50 AX-21/Saran* from 415 Solid Polymer	44.5	55.4	70.0
80/20 AC Carbone/Saran* from 506 Solid Polymer	37.5	44.8	53.3
100 Saran Carbon* from 415 Solid Polymer	56.7	61.4	69.9

*Large disks used in cycling tests

Table 7/ Properties of Carbons Used in Cycling Studies

Carbon	100% Saran	50% Saran 50% AX-21	20% Saran 80% CNS-196
Density g/mL			
Packing	0.93	0.56	0.72
Bulk	1.00	0.62	0.74
Mercury 413.5 MPa (60 000 psi)	1.20	0.93	1.17
Macropore Volume mL/g	0.17	0.54	0.55
Volume Percent Utilization of Storage Vessel			
Carbon	42.3	25.4	32.7
Micropore	35.2	34.8	28.8
Macropore	15.5	30.1	35.8
Void	7.0	9.7	2.7
77 K Nitrogen Isotherm			
Surface Area m ² /g	1000	1600	910
Dubinín Micropore Volume mL/g	0.44	0.69	0.38
25°C Methane Isotherm			
g methane ads. per g carbon			
2.1 MPa (300 psi)	0.091	0.094	0.068
3.4 MPa (500 psi)	0.096	0.113	0.078
6.9 MPa (1000 psi)	0.102	0.140	0.090

Table 8/ Number of Cycles per Test

Pressure	Fill Time	Carbon		
		100% Saran	50% Saran 50% AX-21	20% Saran 80% CNS-196
2.1 MPa (300 psi)	15 min	281	54	50
	4 h	67	--	--
3.4 MPa (500 psi)	15 min	68	50	50
	4 h	85	50	20
6.9 MPa (1000 psi)	15 min	105	52	--
	4 h	80	--	--

2 h empty for all tests

Table 9/ Amount of Natural Gas Stored in Vessel (g/L)

Carbon	Cycle #	Pressure (MPa)					
		2.1		3.4		6.9	
		Fill Time (h)					
		0.25	4.0	0.25	4.0	0.25	4.0
100% Saran	1	81.1	84.2	91.6	94.3	99.4	101.2
	2	75.5	84.0	86.0	94.6	96.0	104.1
	5	77.1	83.0	87.1	98.2	96.9	106.1
	10	78.4	91.2	90.1	101.7	98.9	110.0
	25	84.9	95.0	93.8	106.7	102.0	113.9
	50	89.2	101.0	97.9	110.9	103.8	117.0
	100	88.9					
	200	91.2					
	280	90.9					
50% Saran							
50% AX-21	1	71.4		85.2	85.4	115.0	
	2	65.7		78.4	87.1	111.3	
	5	68.7		79.8	89.6	113.6	
	10	71.6		81.5	91.8	113.9	
	25	76.2		86.2	95.5	118.4	
	50	78.7		88.9	99.0	118.6	
20% Saran							
80% CNS-196	1	63.4		76.7	77.1		
	2	59.8		72.6	80.3		
	5	61.4		75.8	79.7		
	10	62.1		77.7	83.3		
	25	66.4		82.6			
	50	69.4		86.1			

Table 10/ Amount of Natural Gas Delivered from Vessel (g/L)

Carbon	Cycle #	Pressure (MPa)					
		2.1		3.4		6.9	
		Fill Time (h)					
		0.25	4.0	0.25	4.0	0.25	4.0
100% Saran	1	52.8	56.8	63.5	67.1	74.7	76.9
	2	47.5	55.4	58.0	64.5	71.3	76.7
	5	46.5	54.5	56.3	63.8	69.4	75.3
	10	46.2	54.8	55.4	61.8	67.6	73.5
	25	45.3	51.5	53.7	59.0	65.9	71.0
	50	44.9	50.2	52.7	58.8	65.2	69.0
	100	44.7					
	200	45.4					
	280	44.4					
50% Saran							
50% AX-21	1	54.4		70.0	70.7	98.2	
	2	47.8		62.5	70.9	93.6	
	5	47.9		61.3	70.2	92.6	
	10	47.8		60.5	69.5	91.4	
	25	47.2		60.3	69.1	88.8	
	50	47.0		60.9	68.9	88.3	
20% Saran							
80% CNS-196	1	46.6		55.9	55.6		
	2	42.8		51.1	57.2		
	5	42.3		50.6	56.1		
	10	41.2		50.0	55.8		
	25	40.9		48.7			
	50	40.1		48.3			

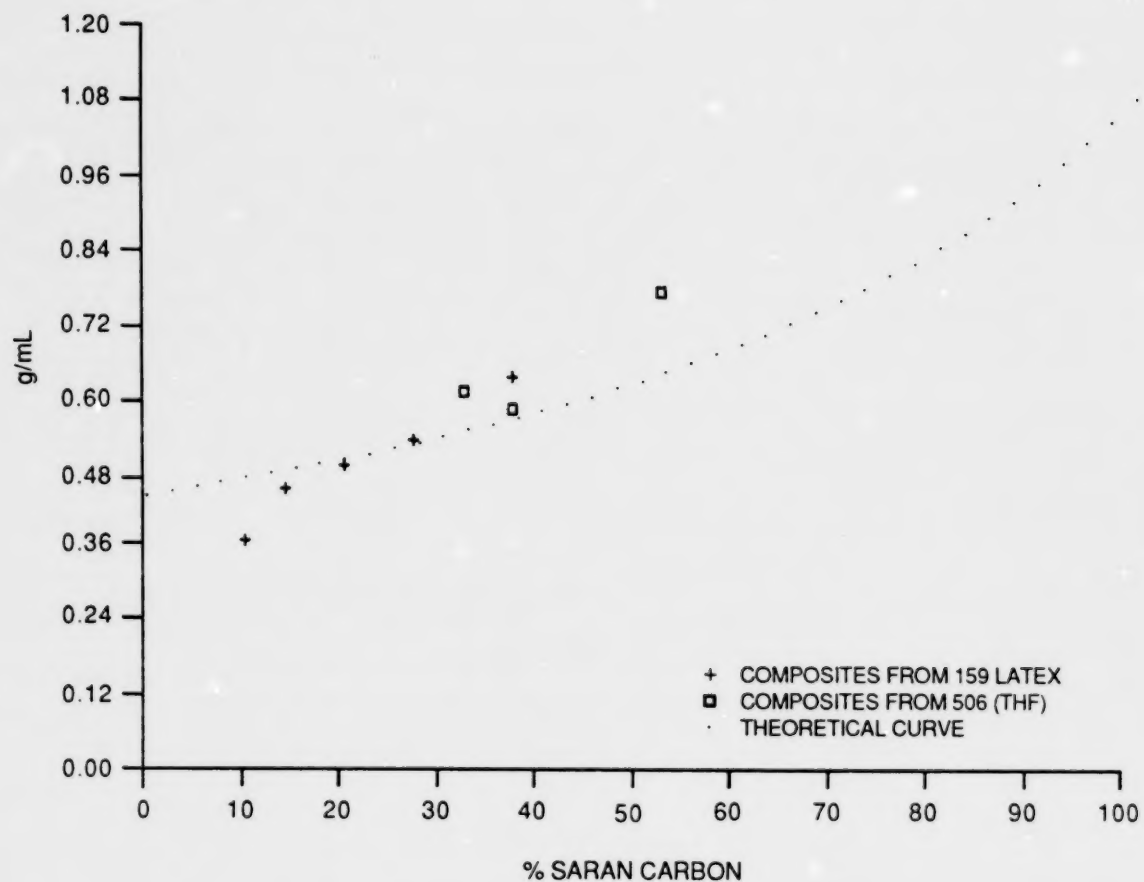


Figure 1/ Packing Density of AX-21/Saran Carbon Composites

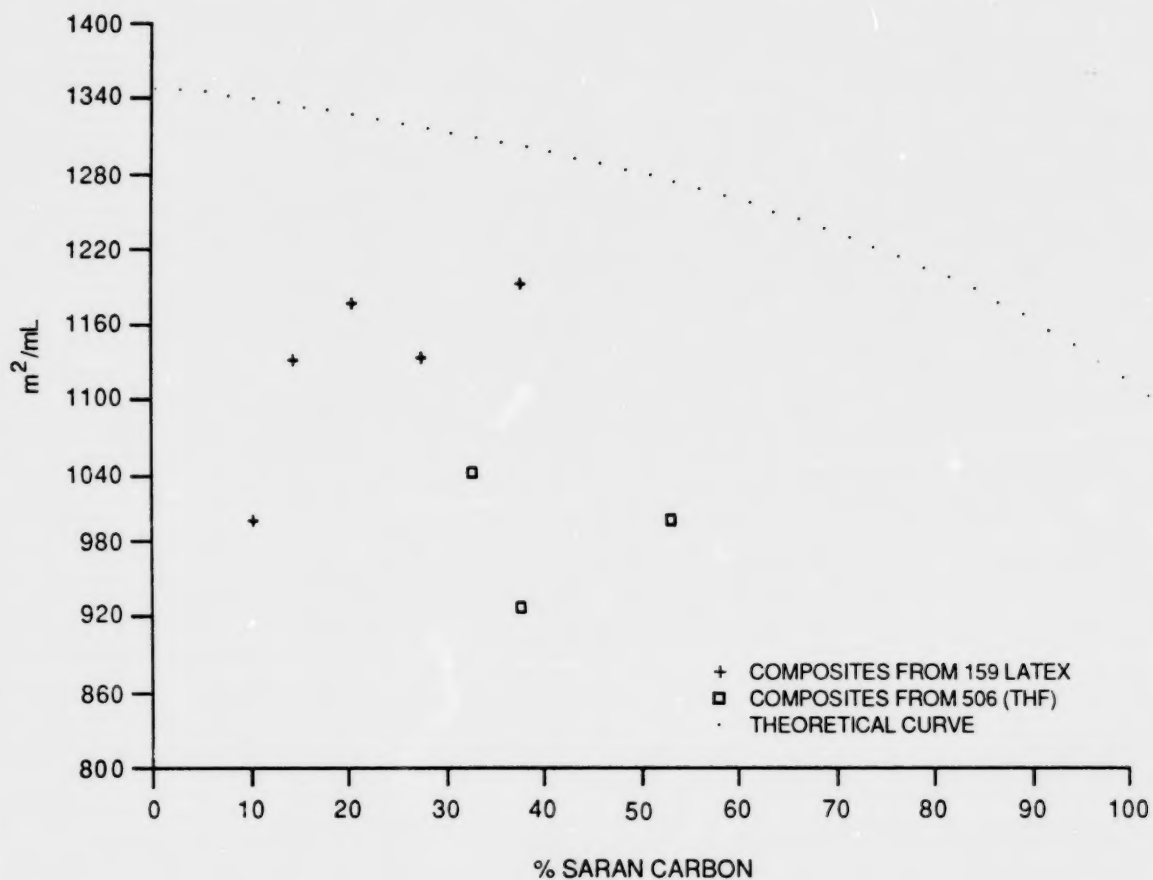


Figure 2/ BET Surface Areas per Unit Volume of AX-21/Saran Carbon Composites

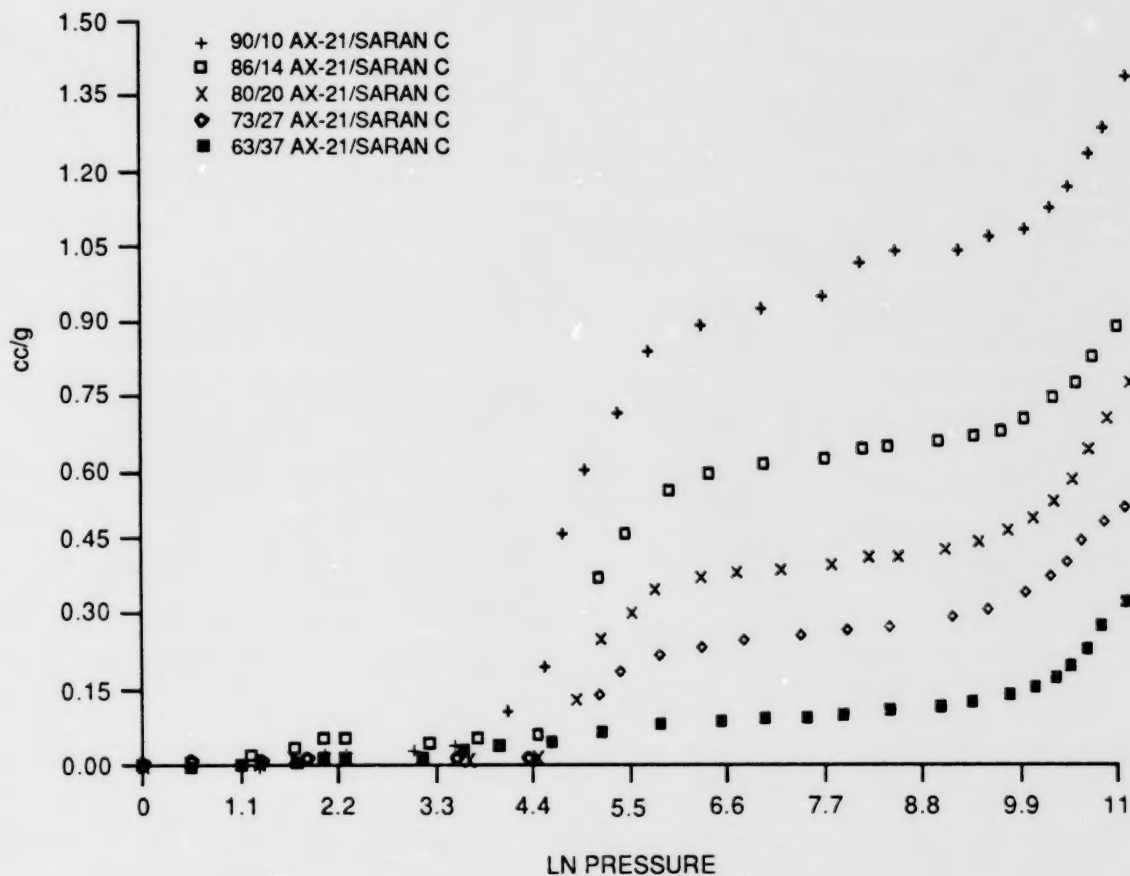


Figure 3/ Mercury Porosimetry Plots of AX-21/Saran Carbon Composites from 159 Latex

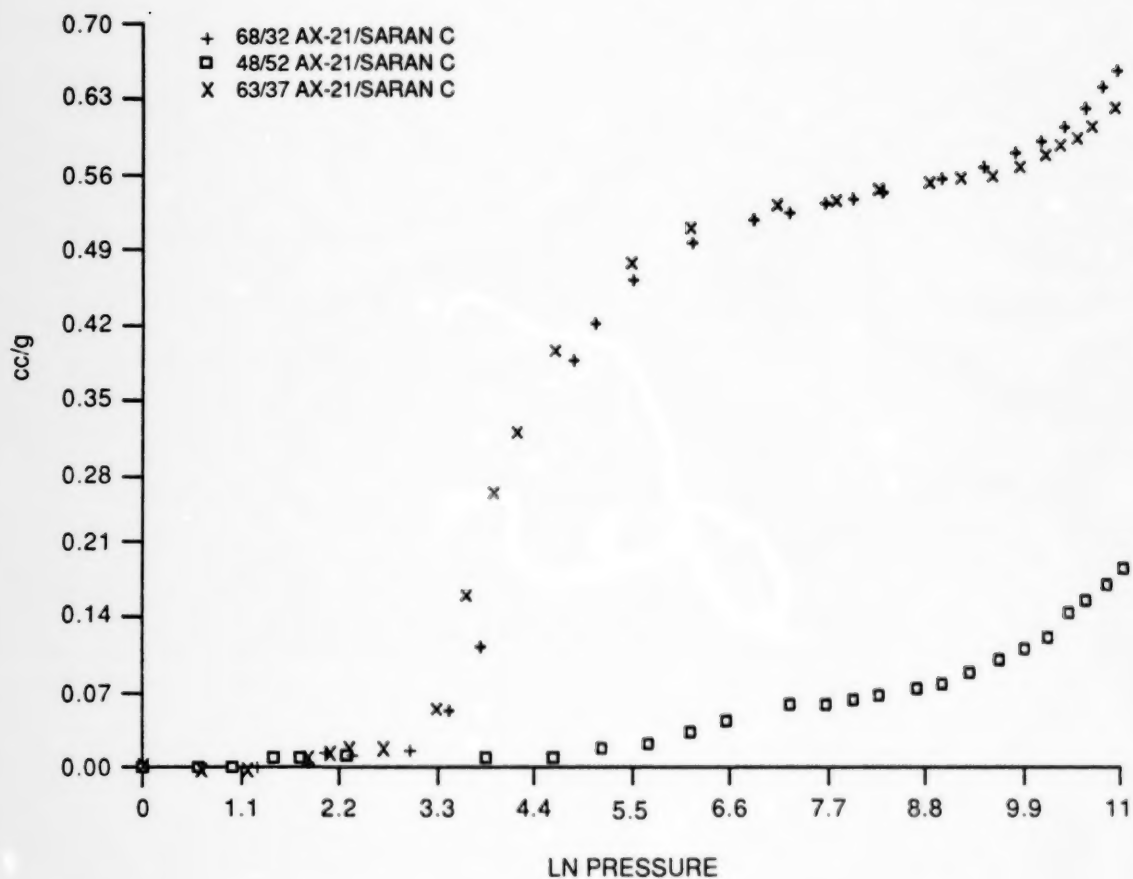


Figure 4/ Mercury Porosimetry Plots of AX-21/Saran Carbon from 506 (THF)

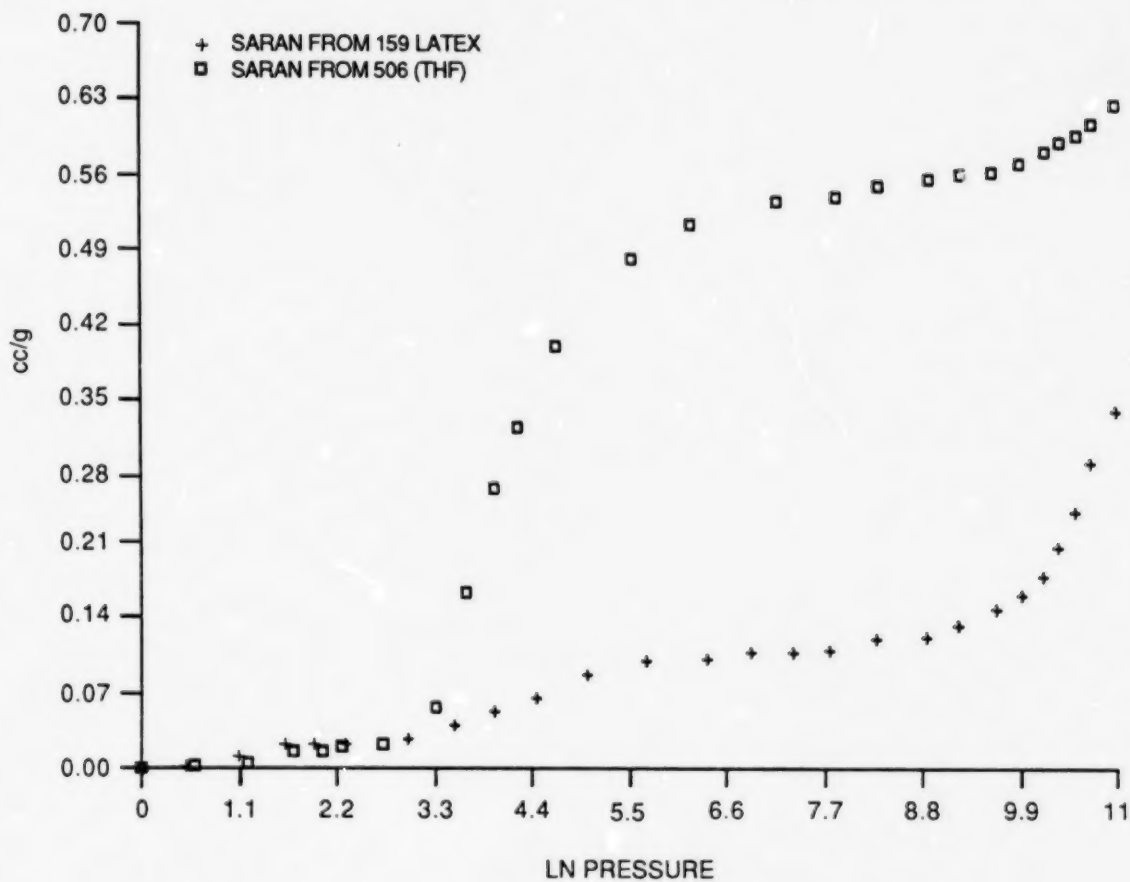


Figure 5/ Mercury Porosimetry Plots of 63/37 AX-21/Saran Carbon

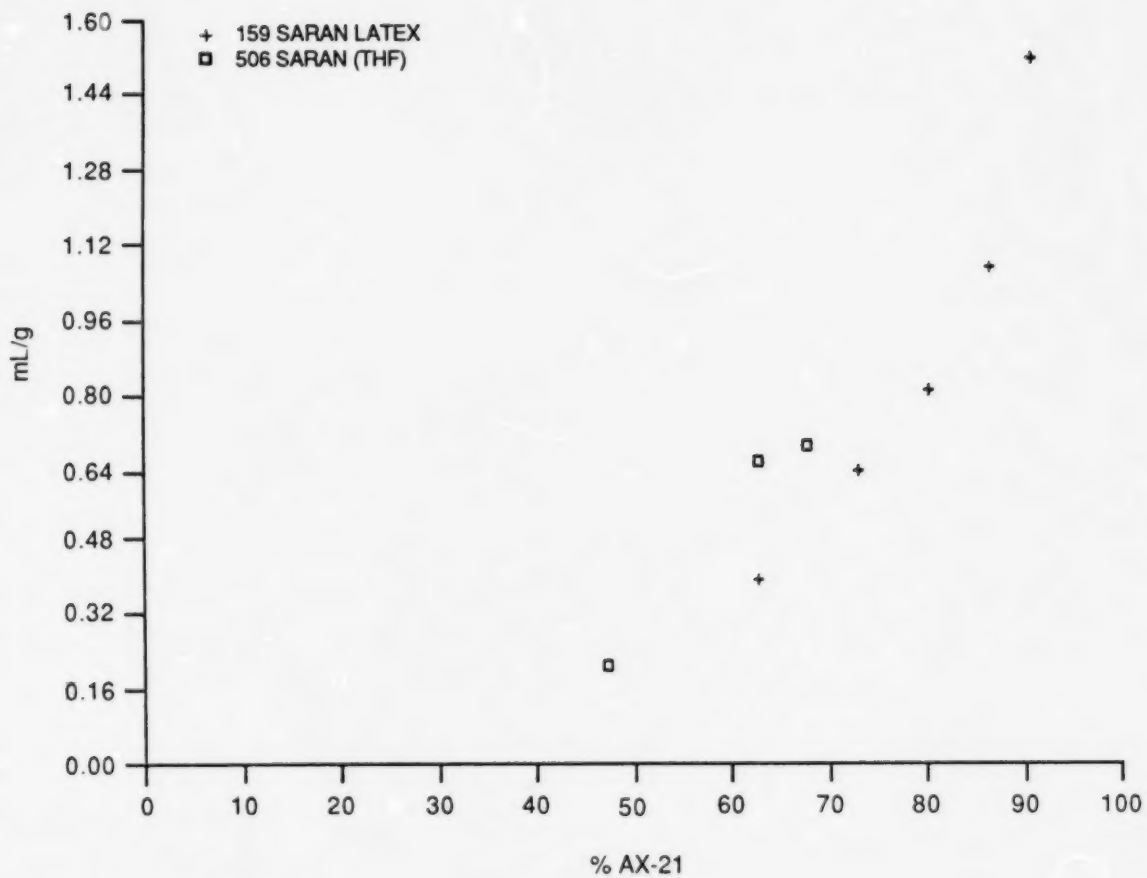


Figure 6/ Macropore Volumes of AX-21/Saran Carbon Composites

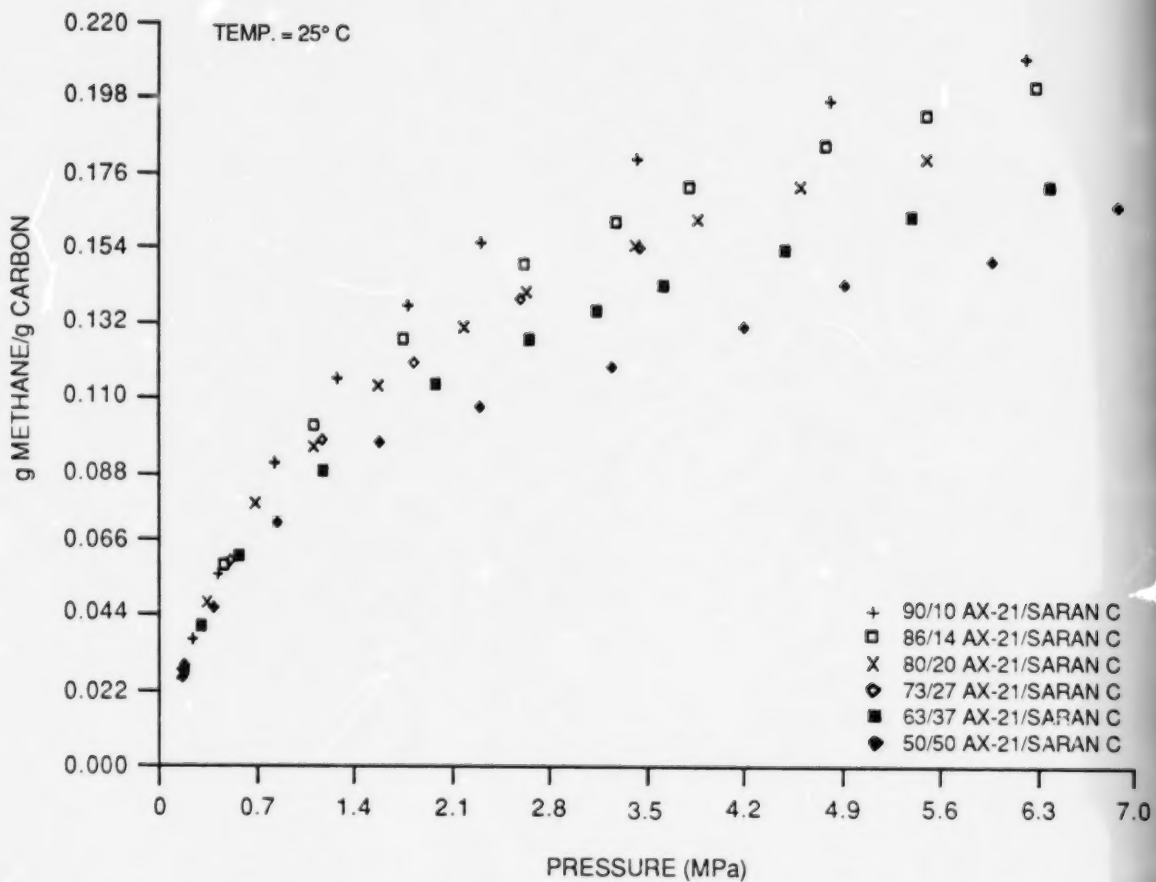


Figure 7/ Mass Basis Methane Adsorption Isotherms of AX-21/Saran Carbon Composites from 159 Latex

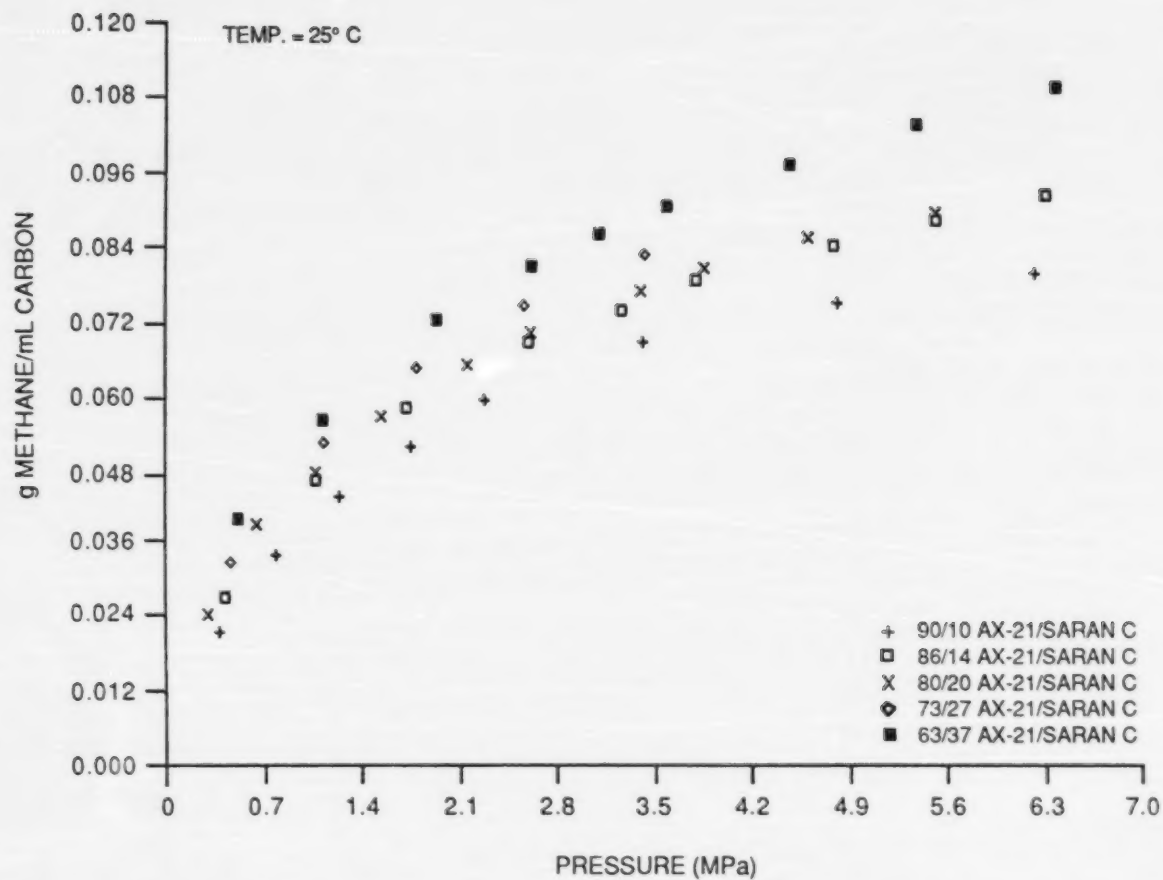


Figure 8/ Volume Basis Methane Adsorption Isotherms of AX-21/Saran Carbon Composites from 159 Latex

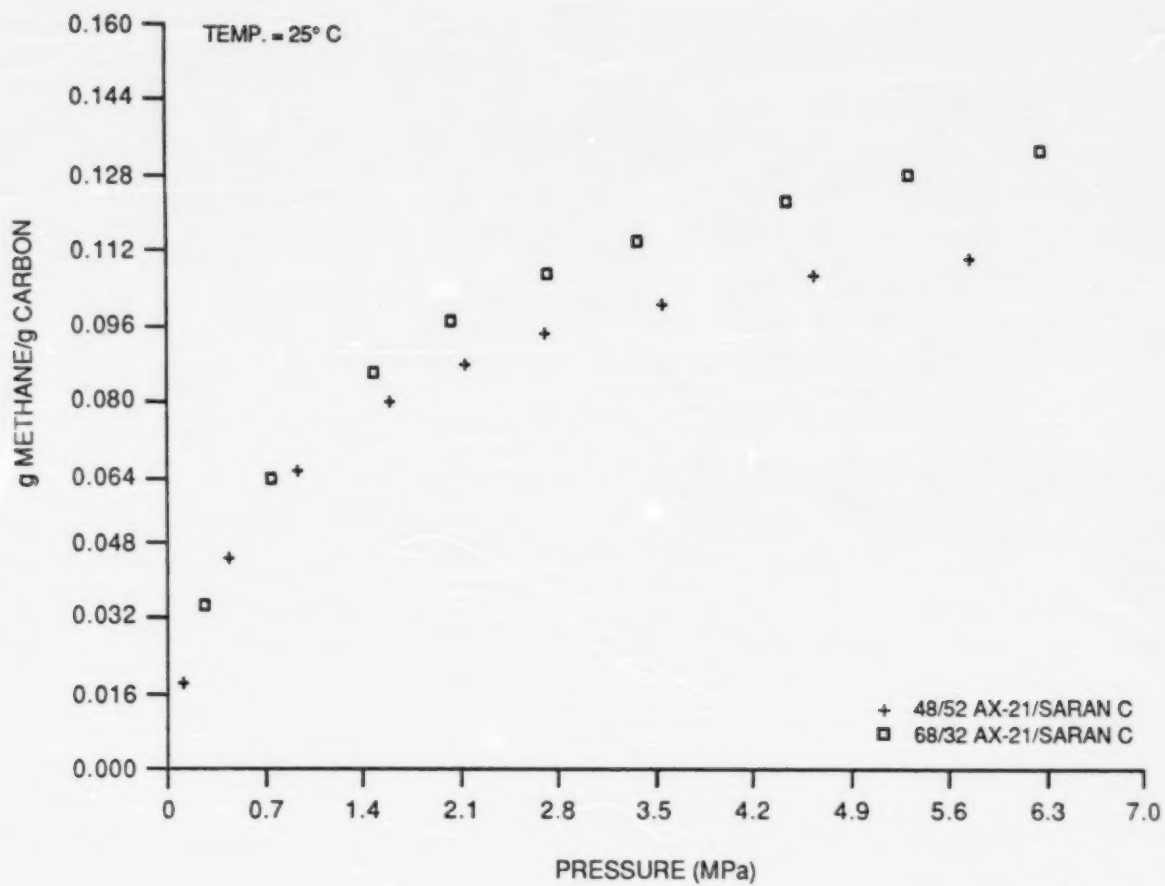


Figure 9/ Mass Basis Methane Adsorption Isotherms of AX-21/Saran Carbon Composites from 506 (THF)

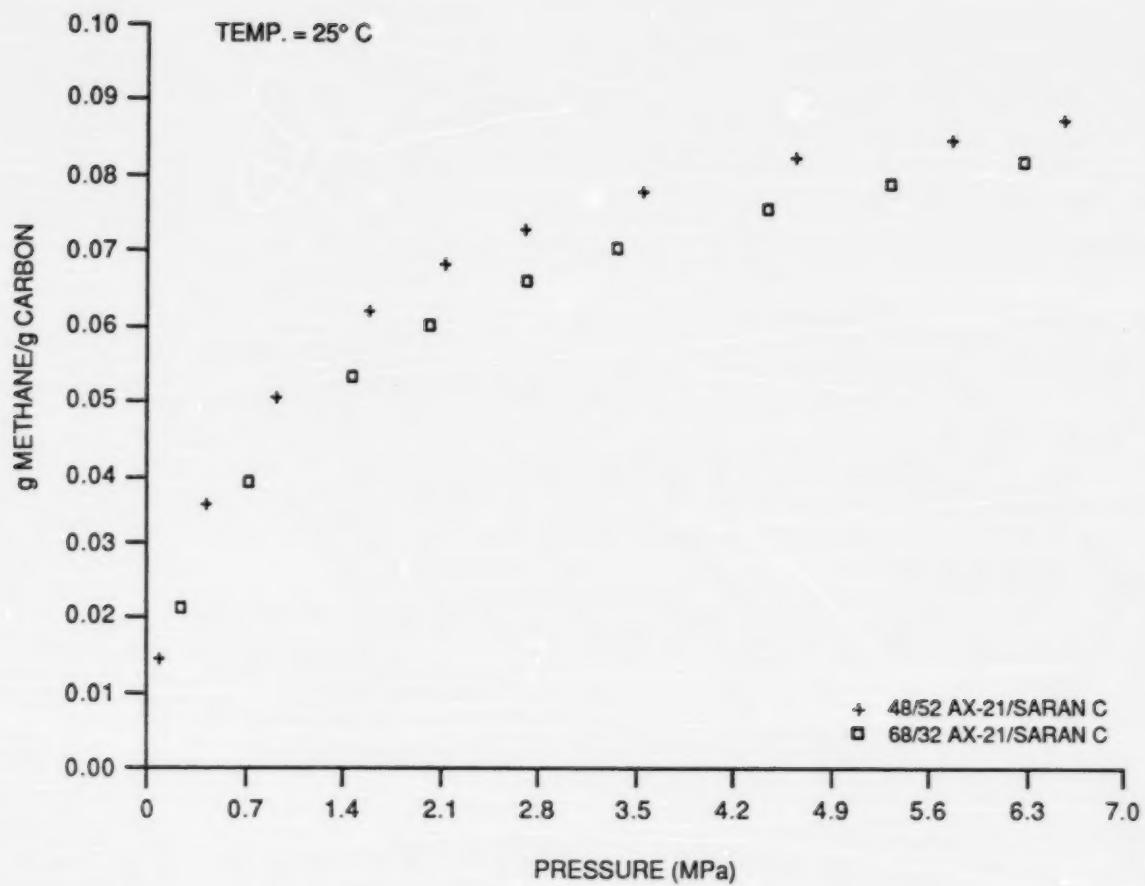


Figure 10/ Volume Basis Methane Adsorption Isotherms of AX-21/Saran Carbon Composites from 506 (THF)

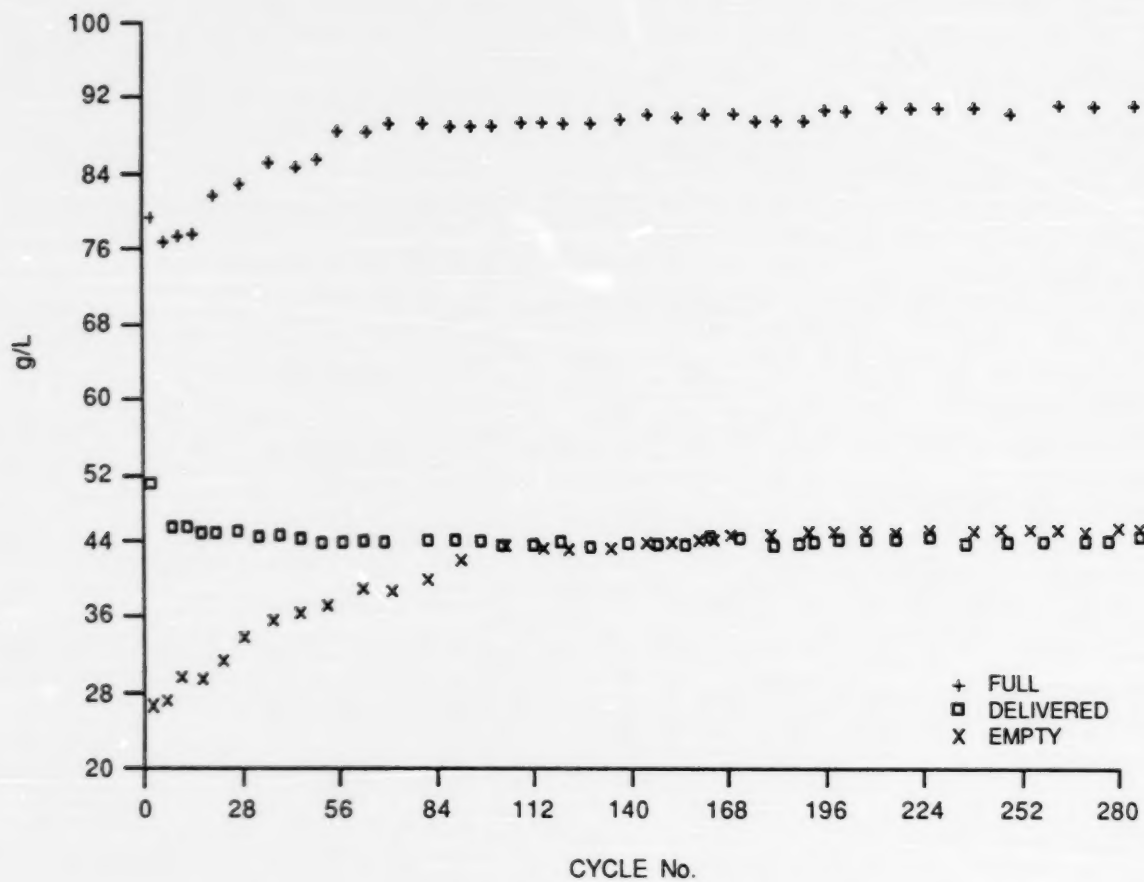


Figure 11/ Cycling Test - Saran Carbon, 2.1 MPa (300 psi) and 15 min Fill

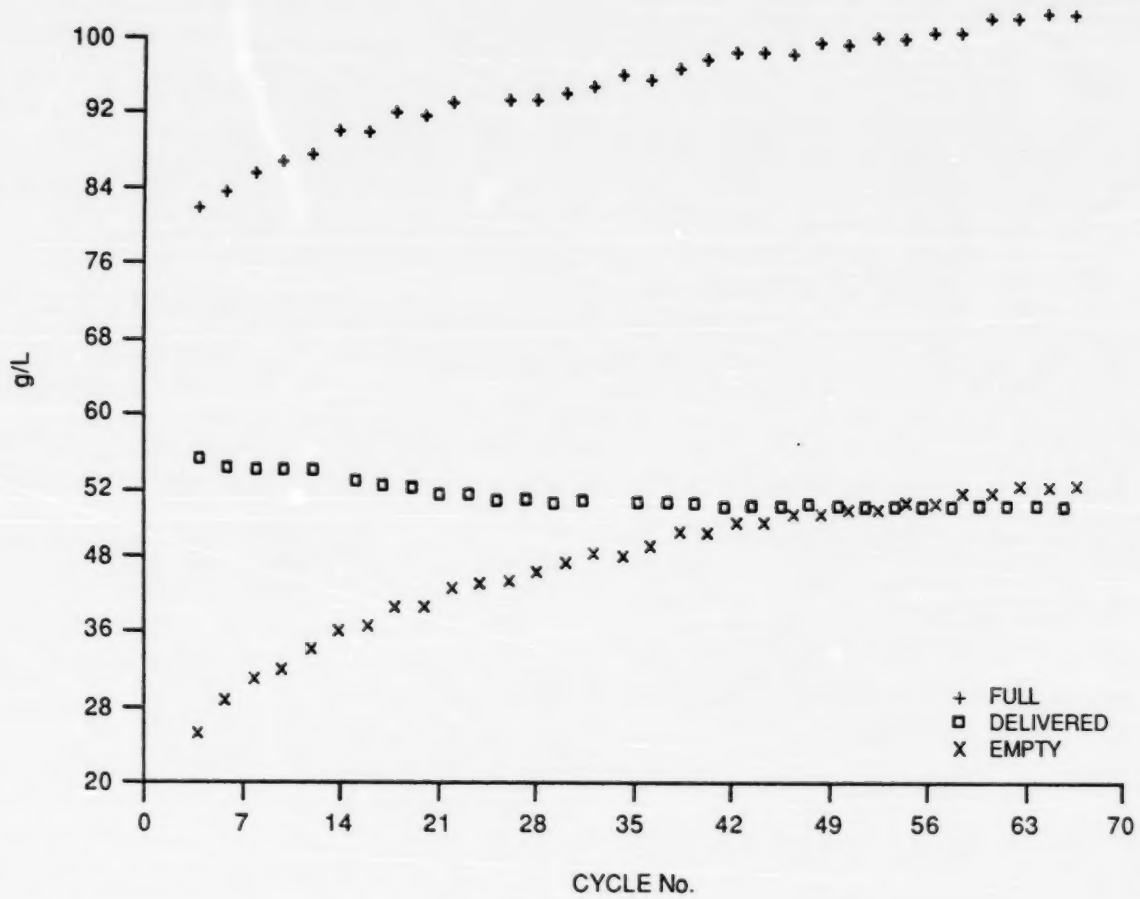


Figure 12/ Cycling Test - Saran Carbon, 2.1 MPa (300 psi) and 4 h Fill

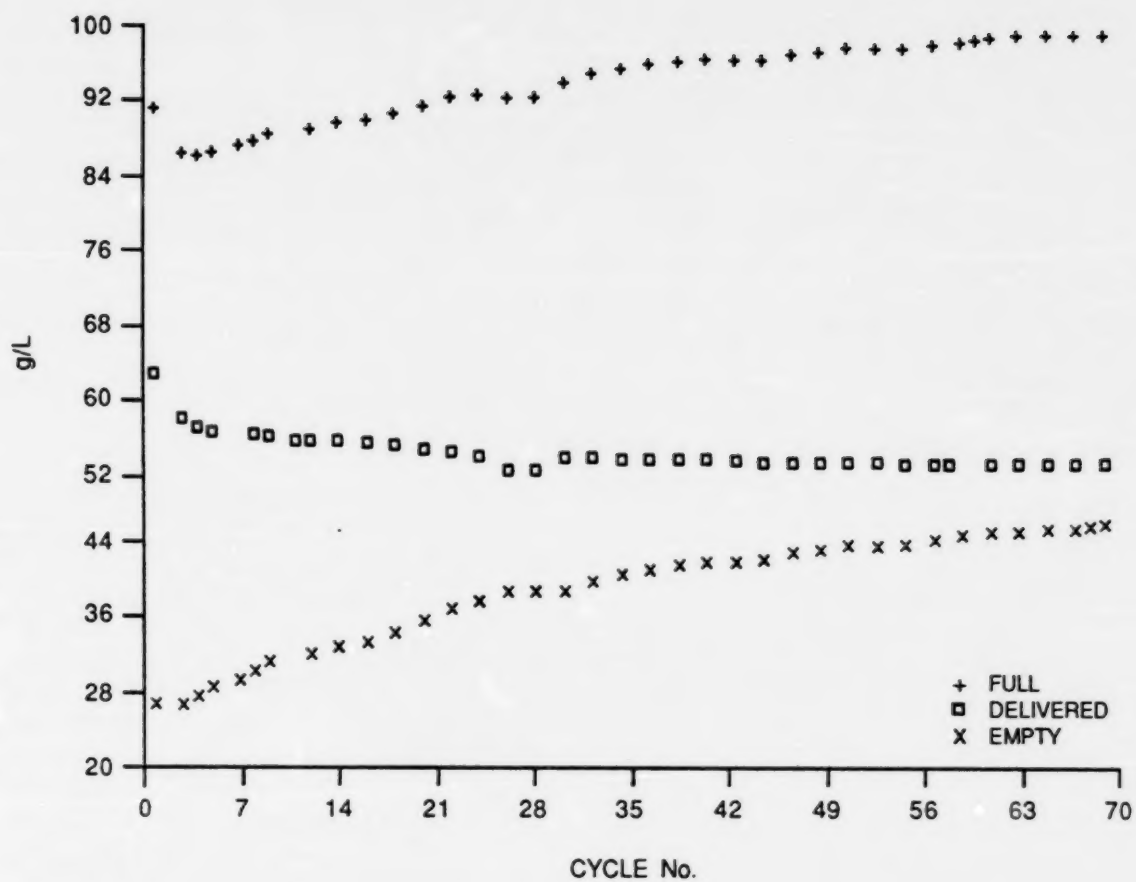


Figure 13/ Cycling Test - Saran Carbon, 3.4 MPa (500 psi) and 15 min Fill

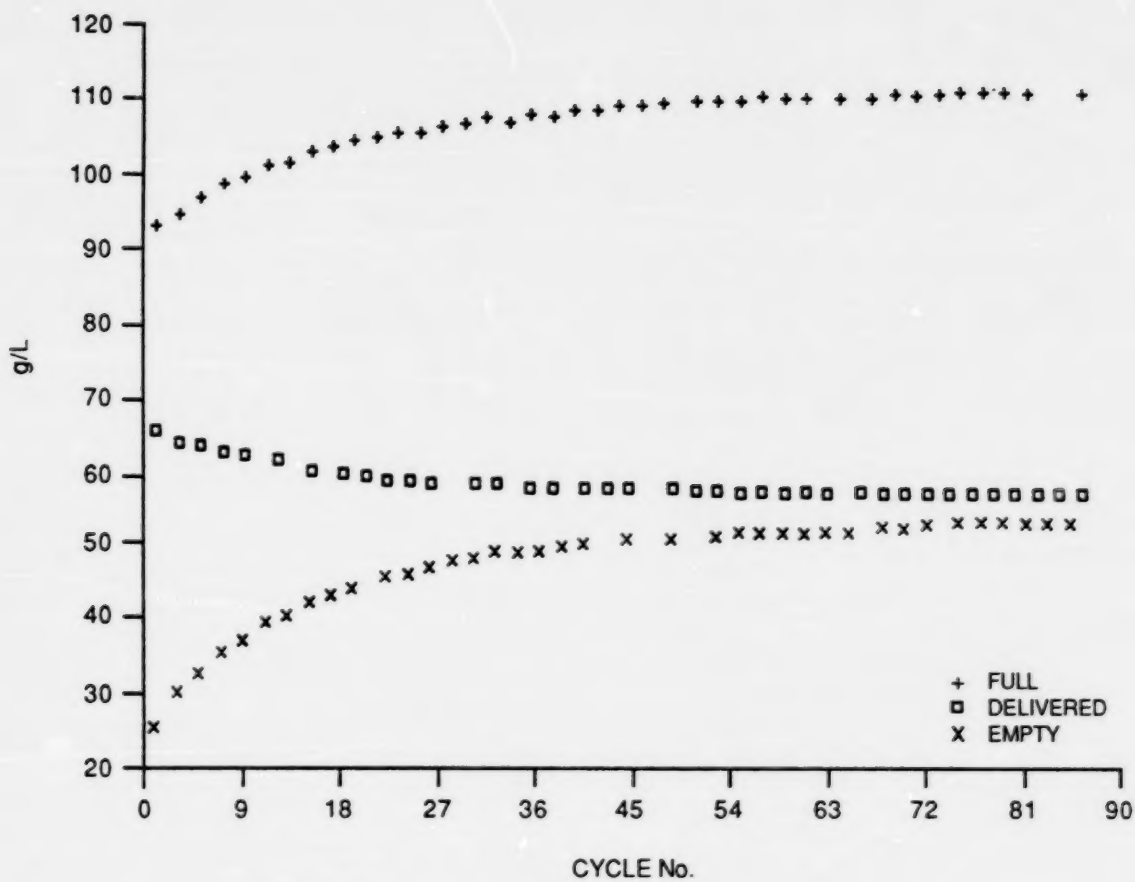


Figure 14/ Cycling Test – Saran Carbon, 3.4 MPa (500 psi) and 4 h Fill

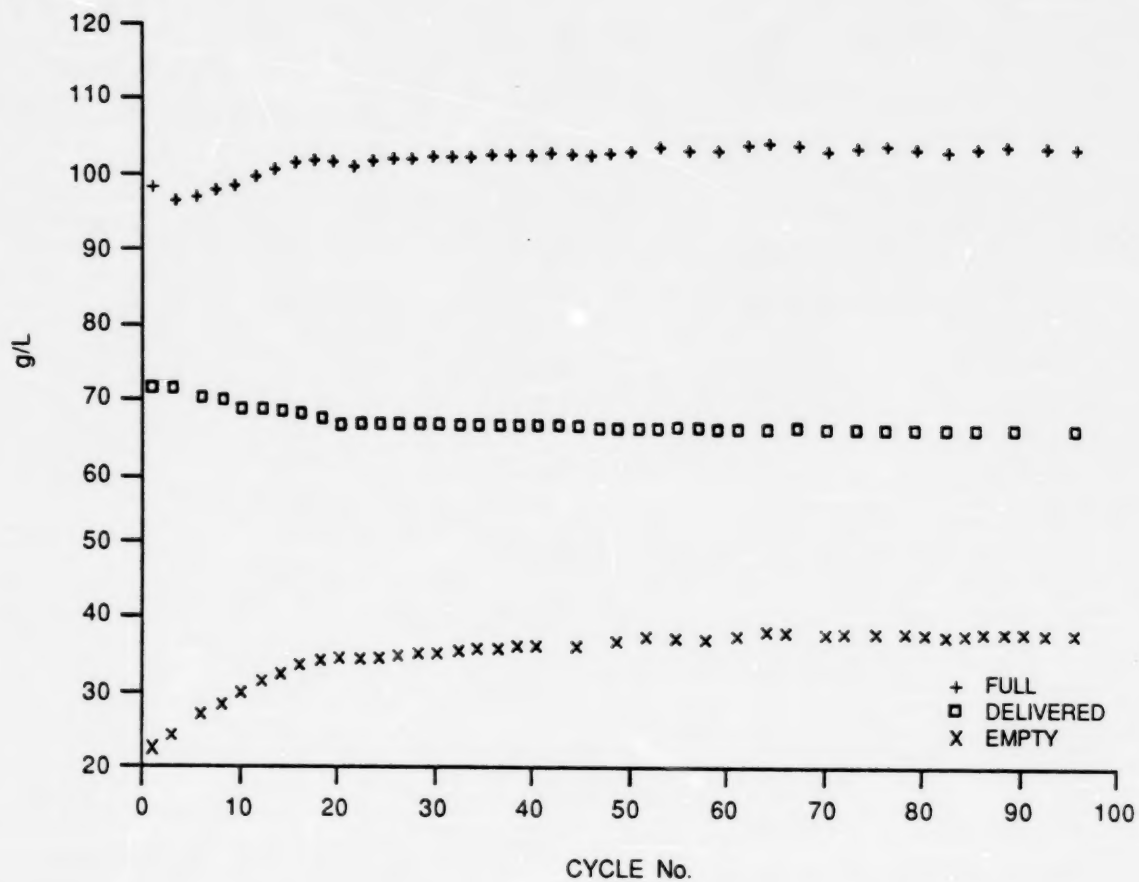


Figure 15/ Cycling Test - Saran Carbon, 6.9 MPa (1000 psi) and 15 min Fill

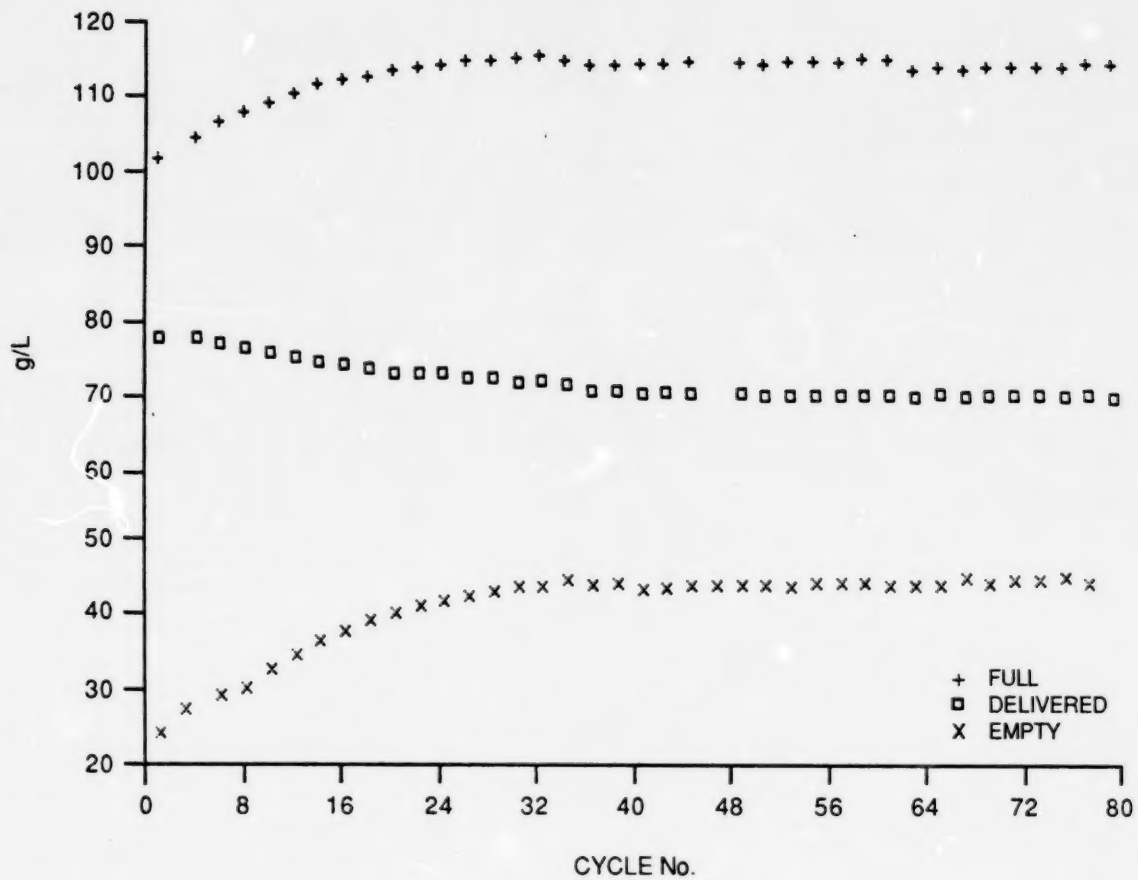


Figure 16/ Cycling Test – Saran Carbon, 6.9 MPa (1000 psi) and 4 h Fill

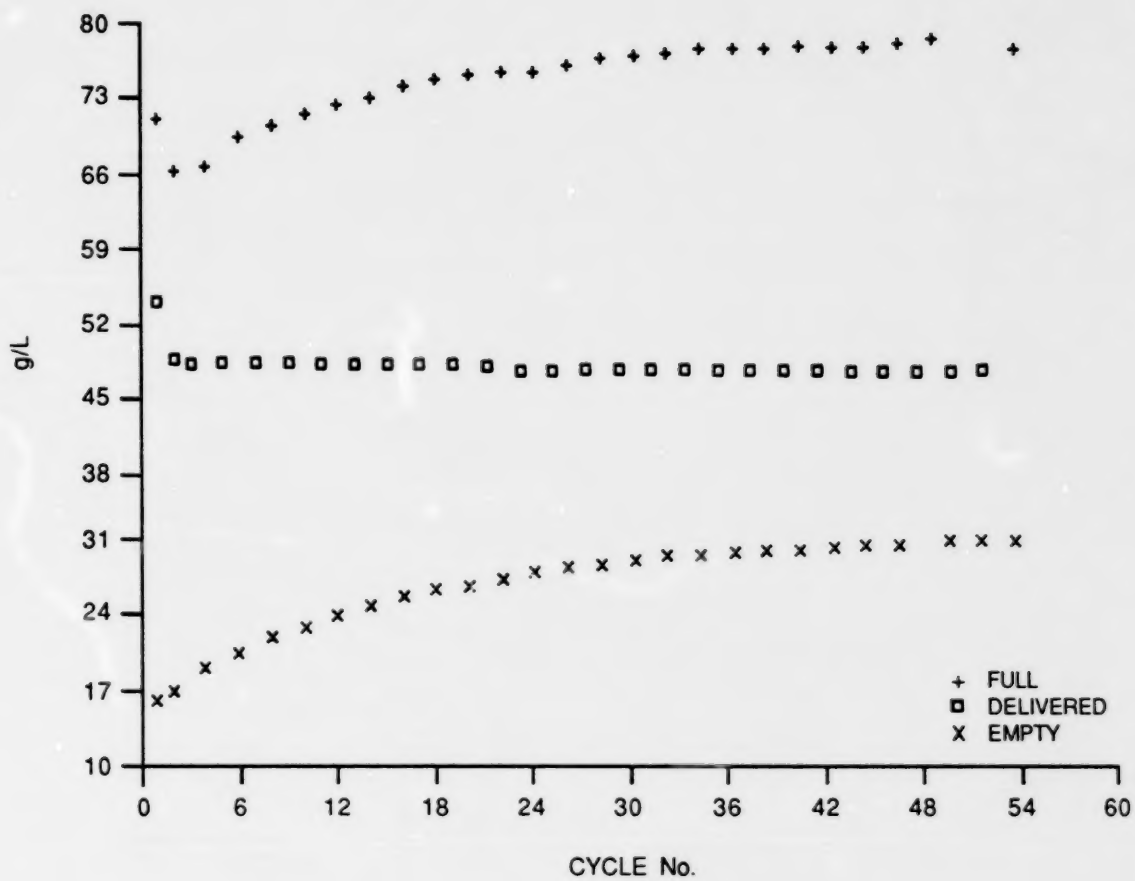


Figure 17/ Cycling Test - 50/50 AX-21/Saran Carbon, 2.1 MPa (300 psi) and 15 min Fill

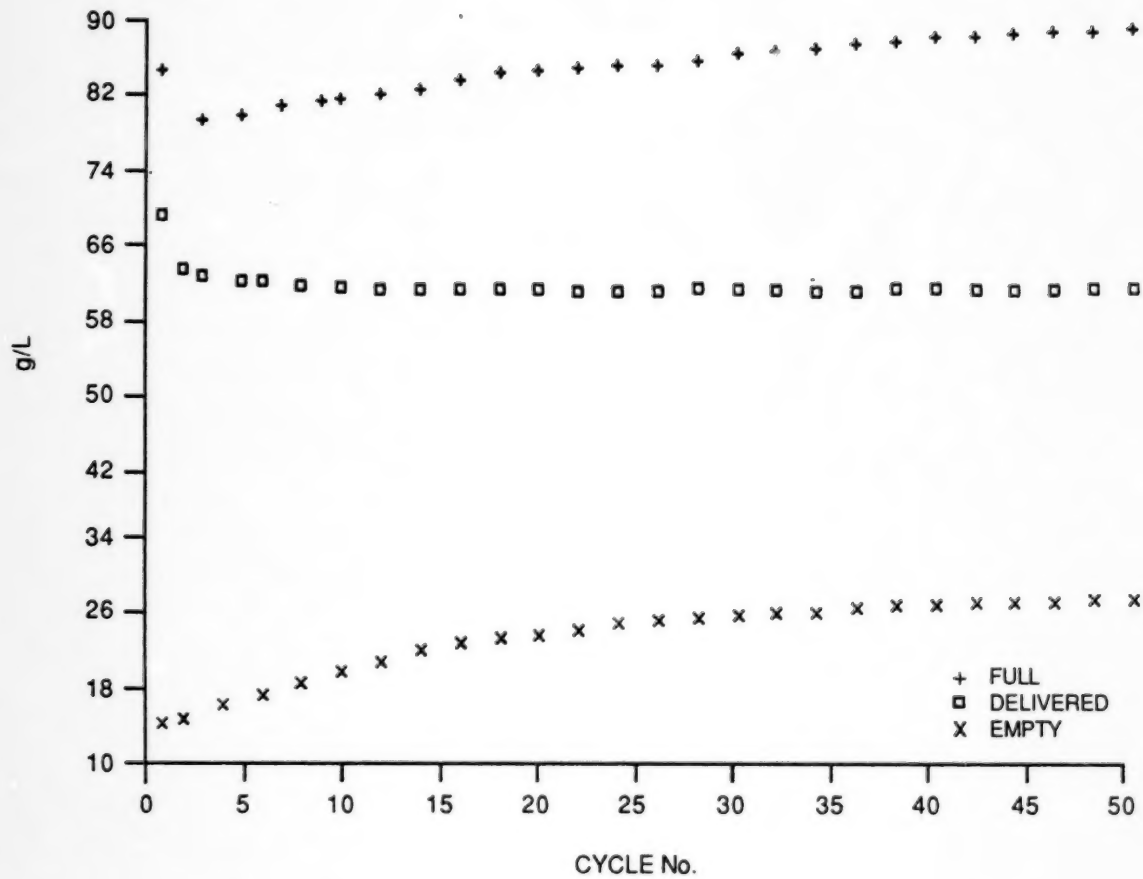


Figure 18/ Cycling Test - 50/50 AX-21/Saran Carbon, 3.4 MPa (500 psi) and 15 min Fill

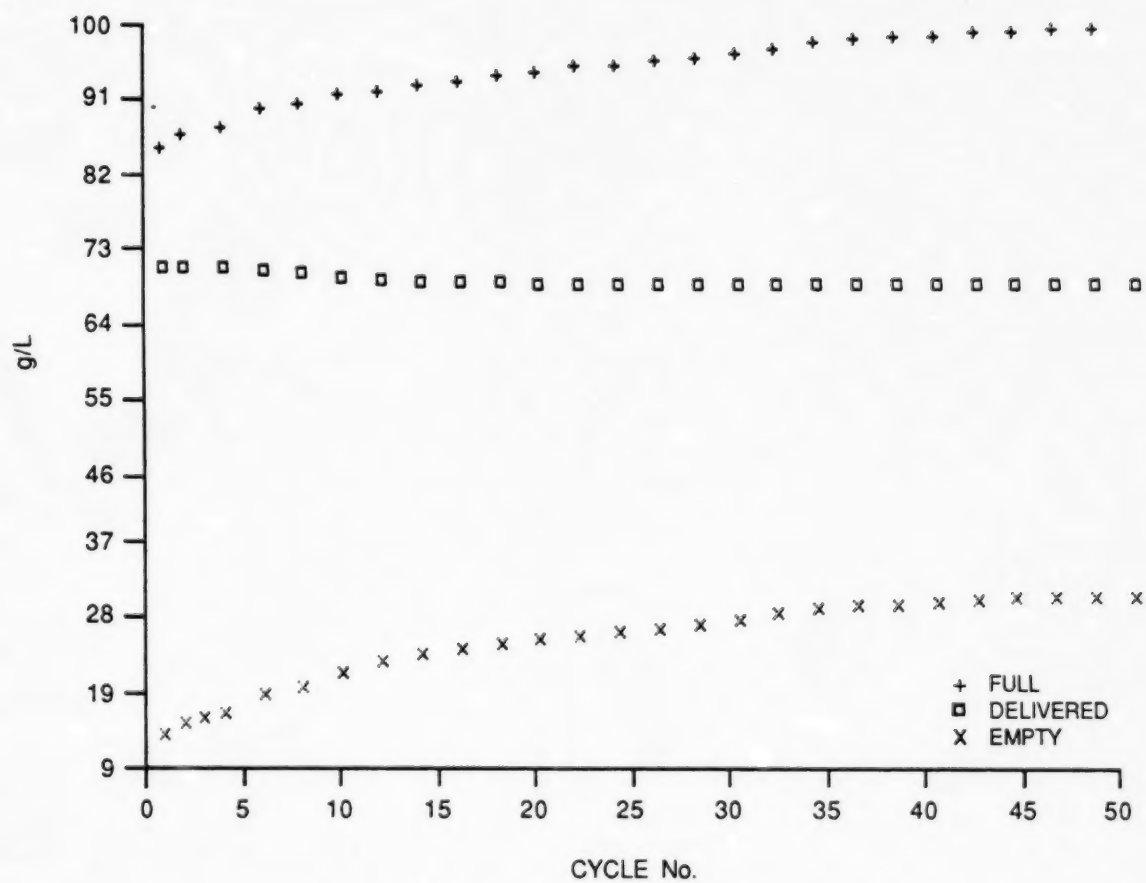


Figure 19/ Cycling Test - 50/50 AX-21/Saran Carbon, 3.4 MPa (500 psi) and 4 h Fill

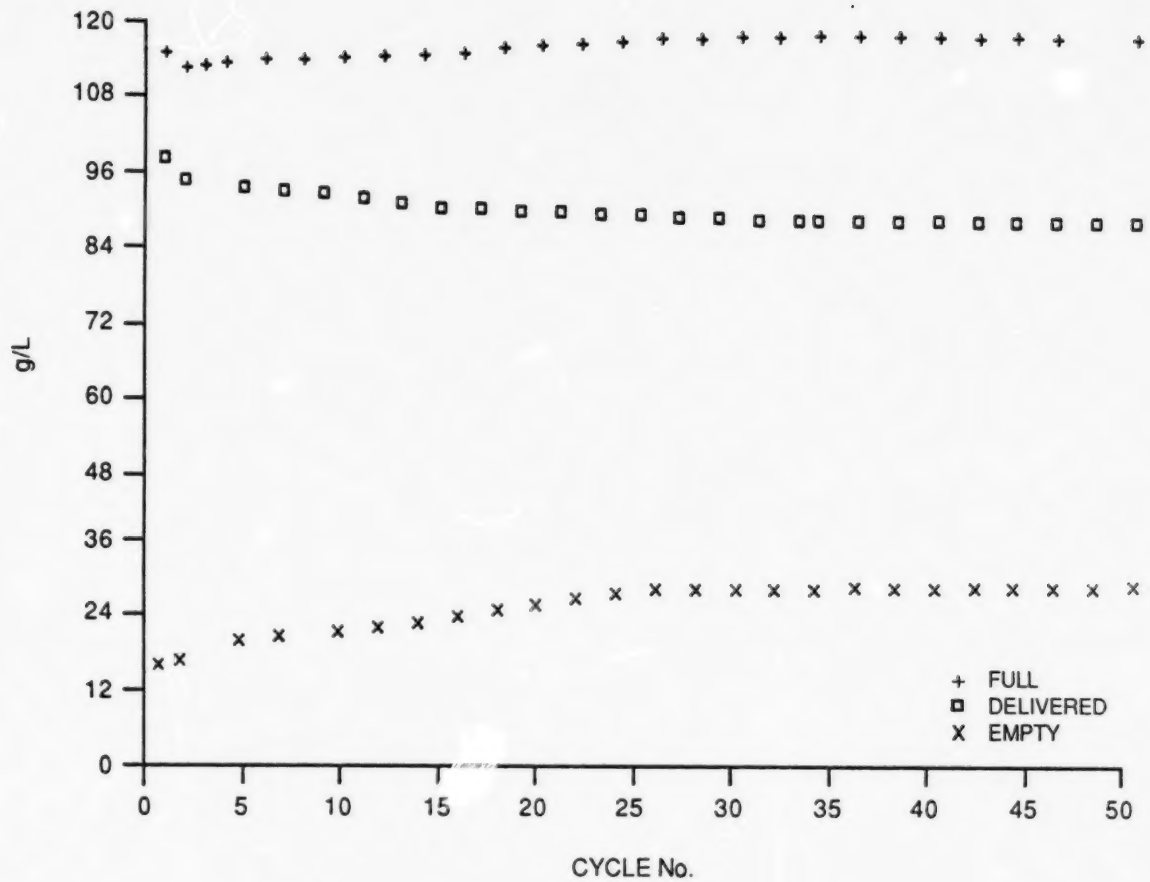


Figure 20/ Cycling Test - 50/50 AX-21/Saran Carbon, 6.9 MPa (1000 psi) and 15 min Fill

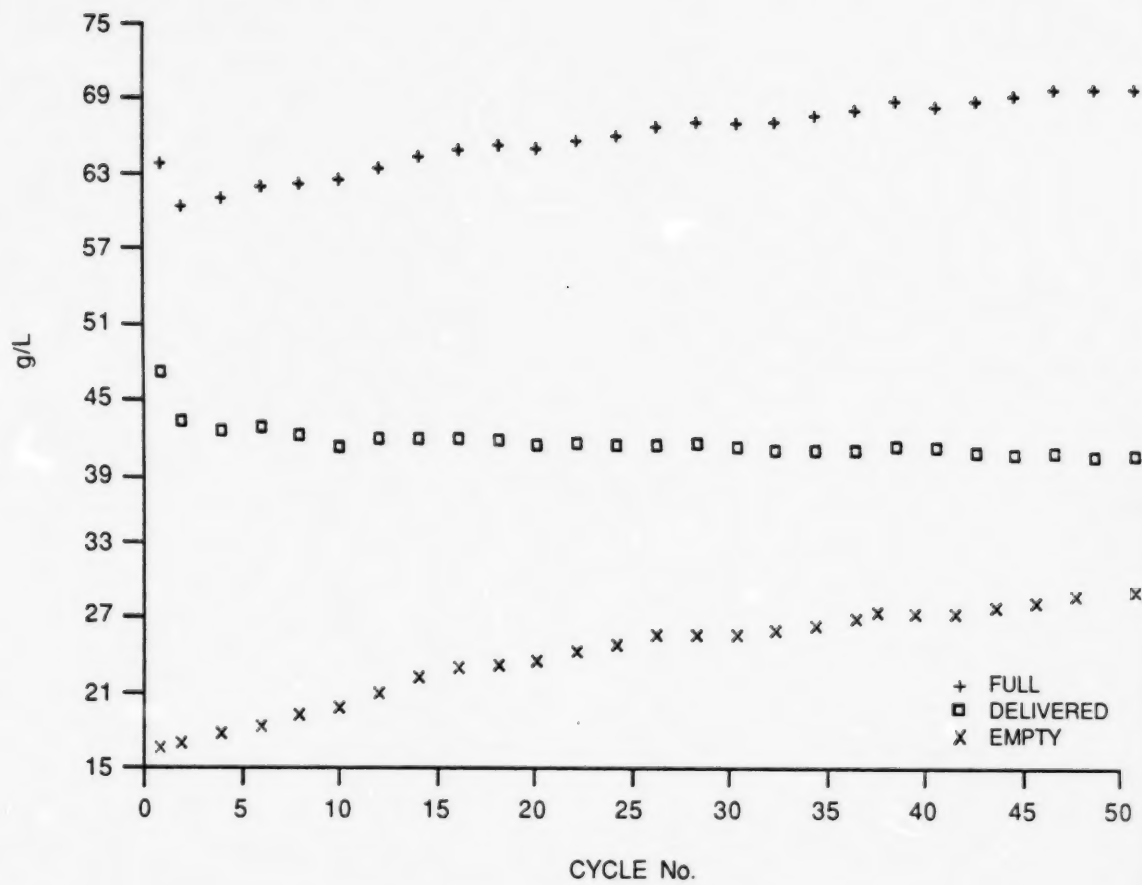


Figure 21/ Cycling Test - 80/20 AC Carbone/Saran Carbon,
2.1 MPa (300 psi) and 15 min Fill

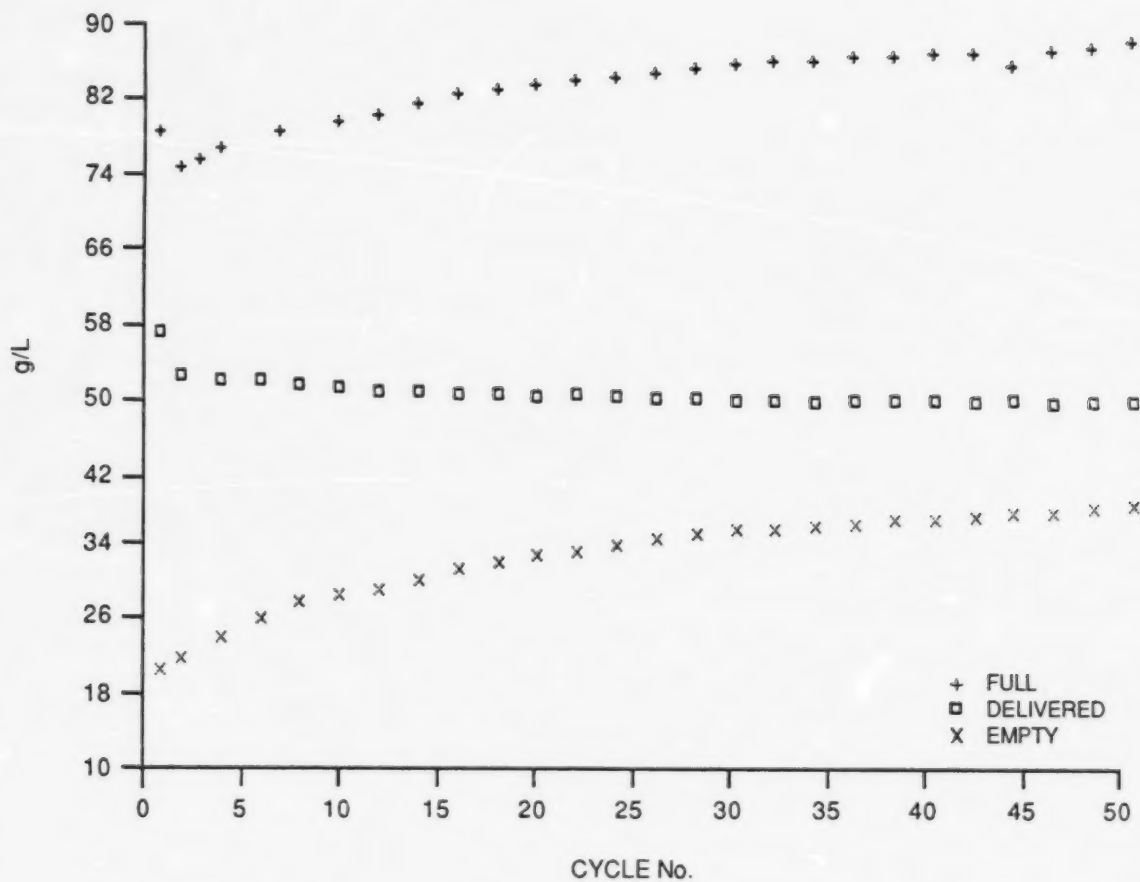


Figure 22/ Cycling Test - 80/20 AC Carbone/Saran Carbon,
3.4 MPa (500 psi) and 15 min Fill

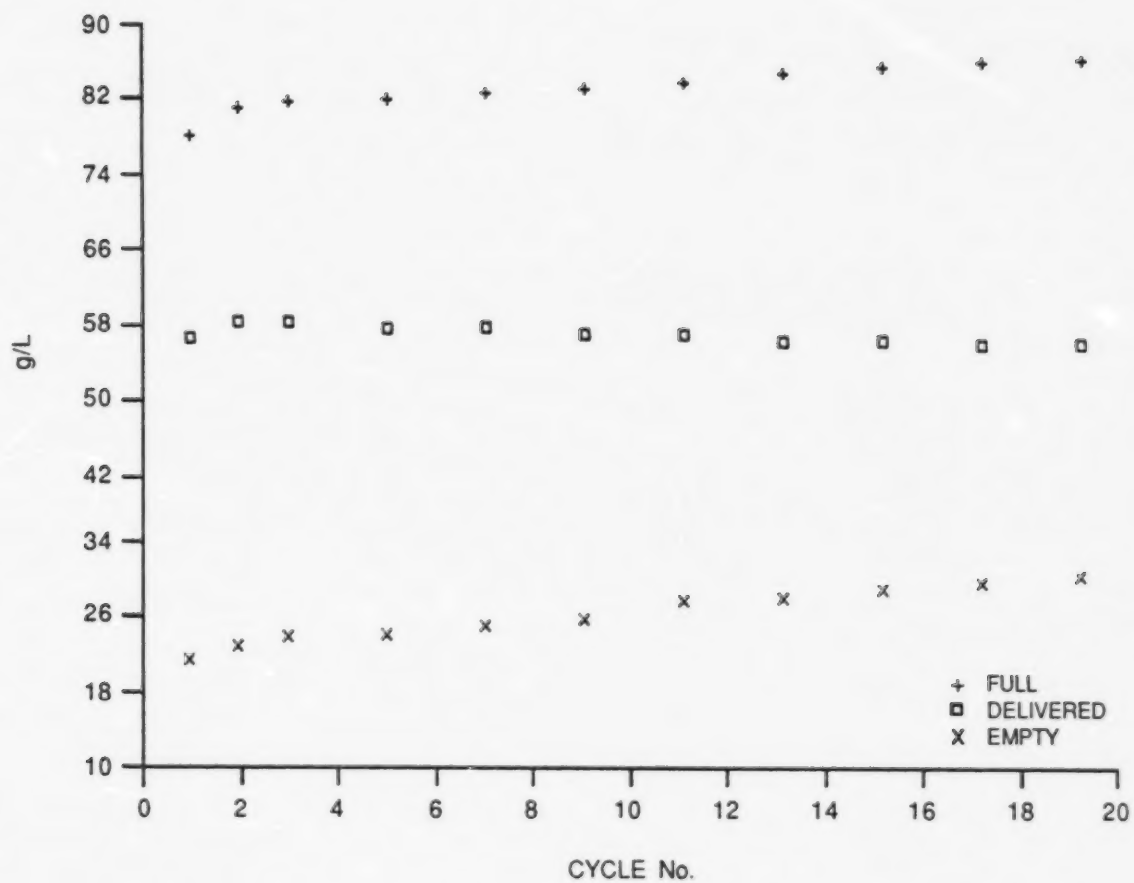


Figure 23/ Cycling Test - 80/20 AC Carbone/Saran Carbon,
3.4 MPa (500 psi) and 4 h Fill

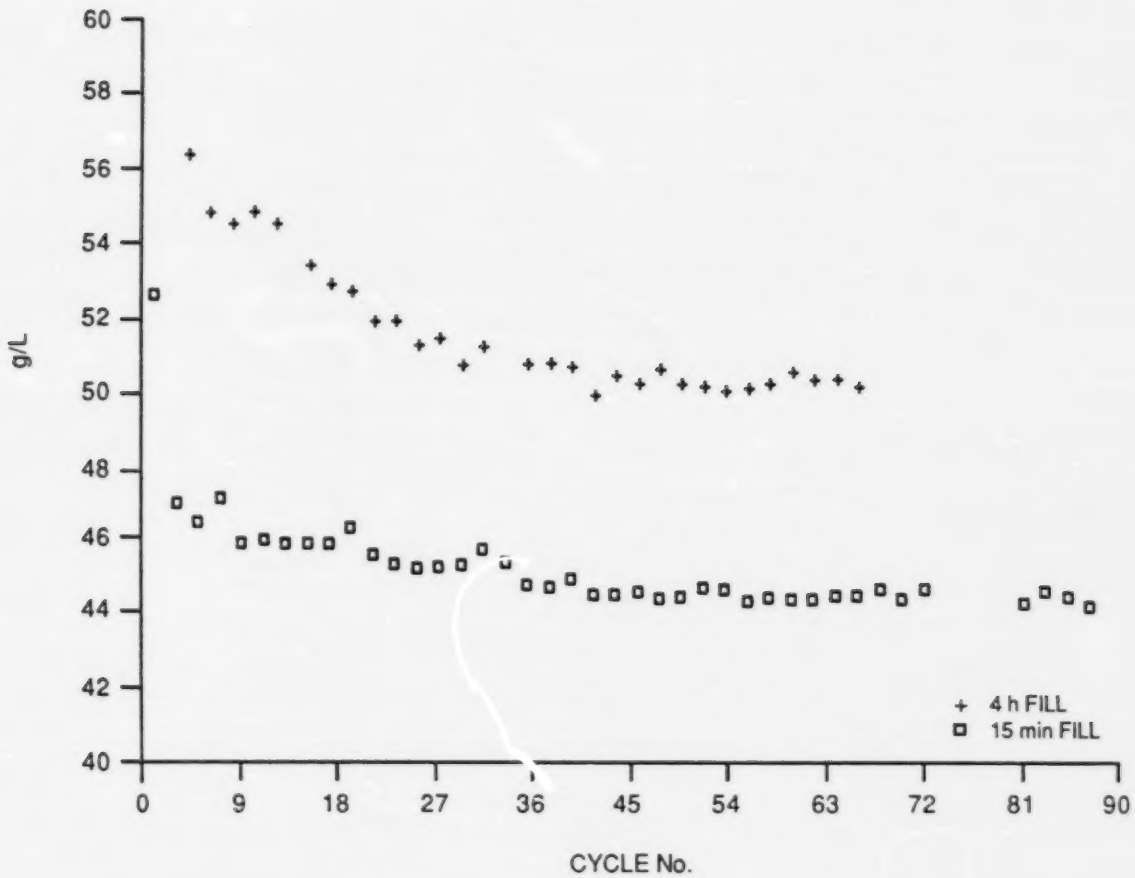


Figure 24/ Cycling Test – Saran Carbon, Amount Delivered at 2.1 MPa (300 psi)

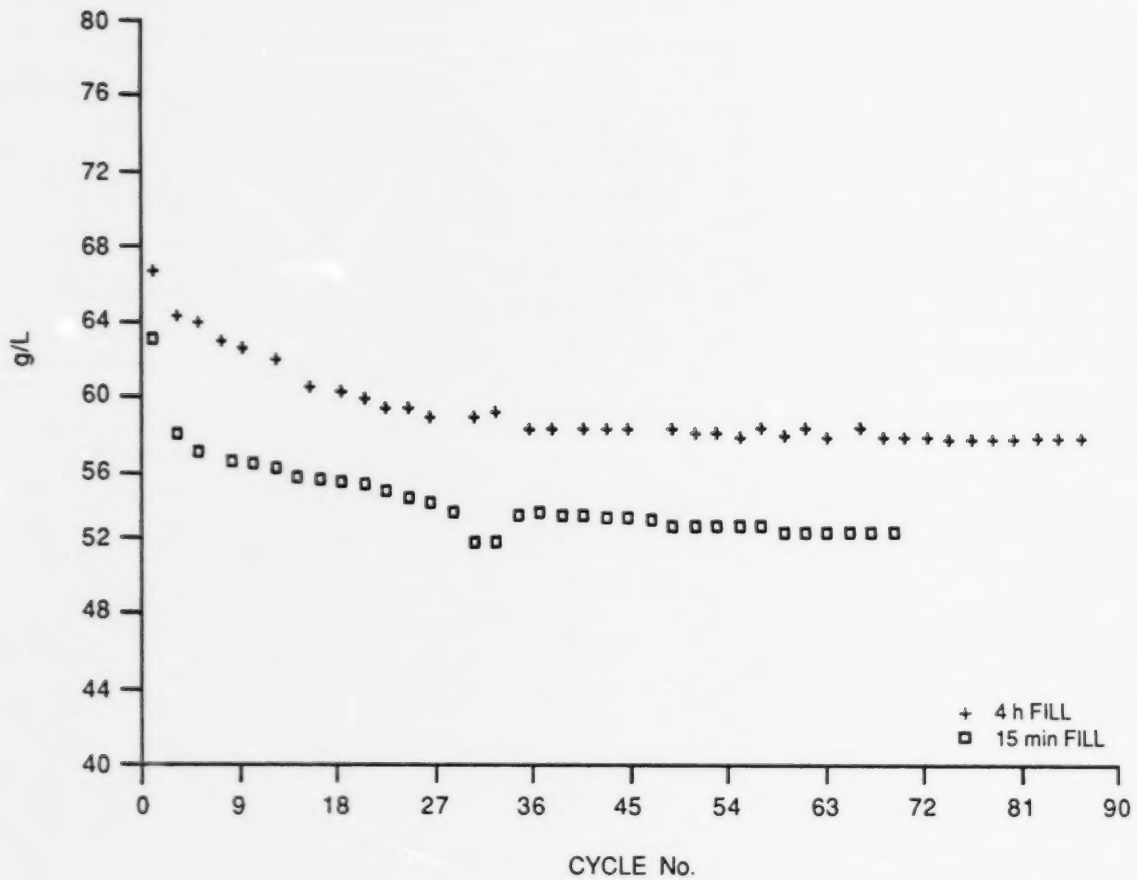


Figure 25/ Cycling Test – Saran Carbon, Amount Delivered at 3.4 MPa (500 psi)

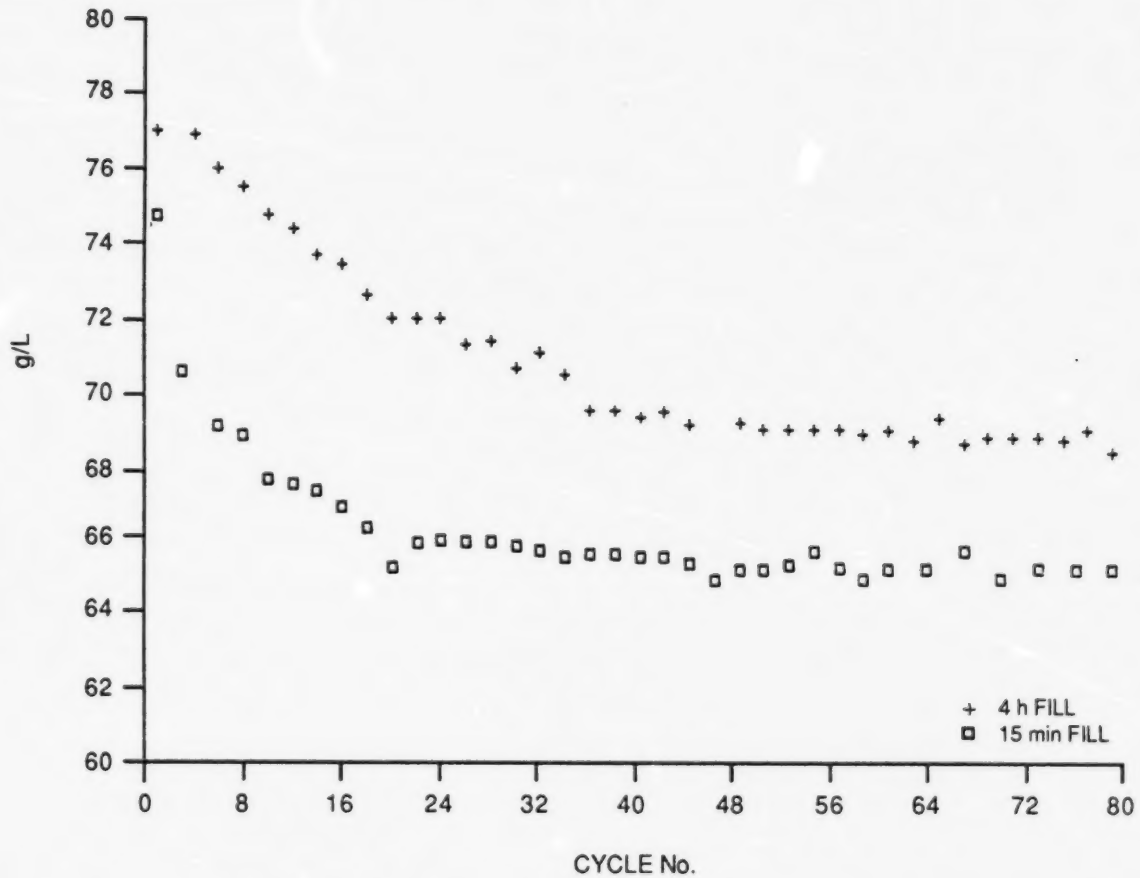


Figure 26/ Cycling Test - Saran Carbon, Amount Delivered at 6.9 MPa (1000 psi)

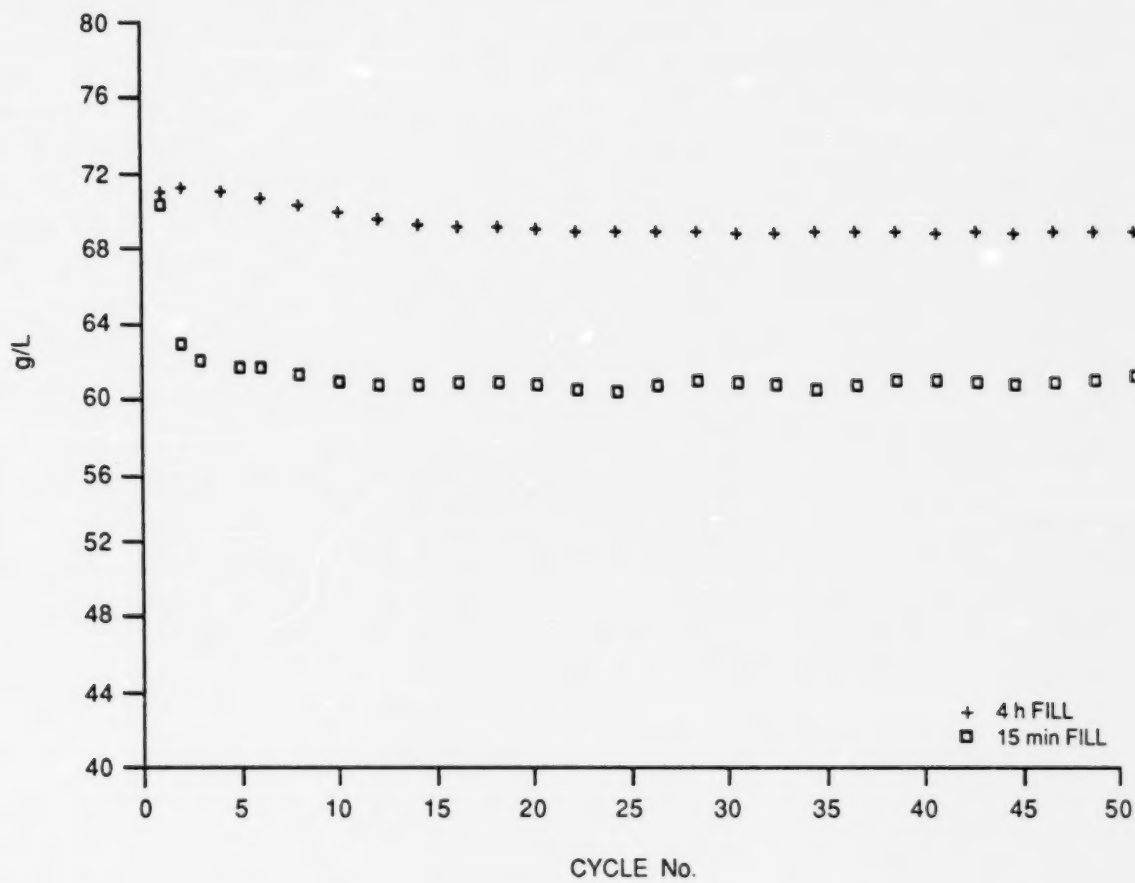


Figure 27/ Cycling Test - 50/50 AX-21/Saran Carbon, Amount Delivered at 3.4 MPa (500 psi)

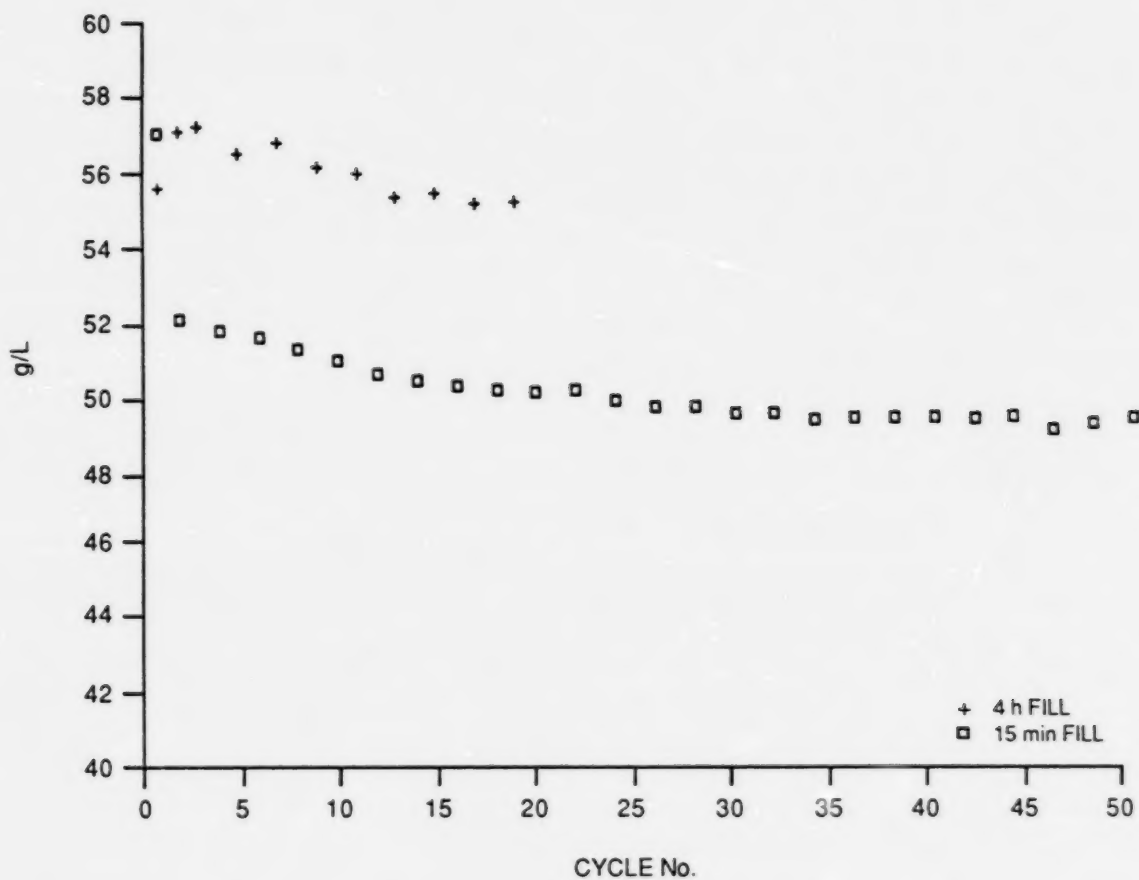


Figure 28/ Cycling Test - 80/20 AC Carbone/Saran Carbon, Amount Delivered at 3.4 MPa (500 psi)

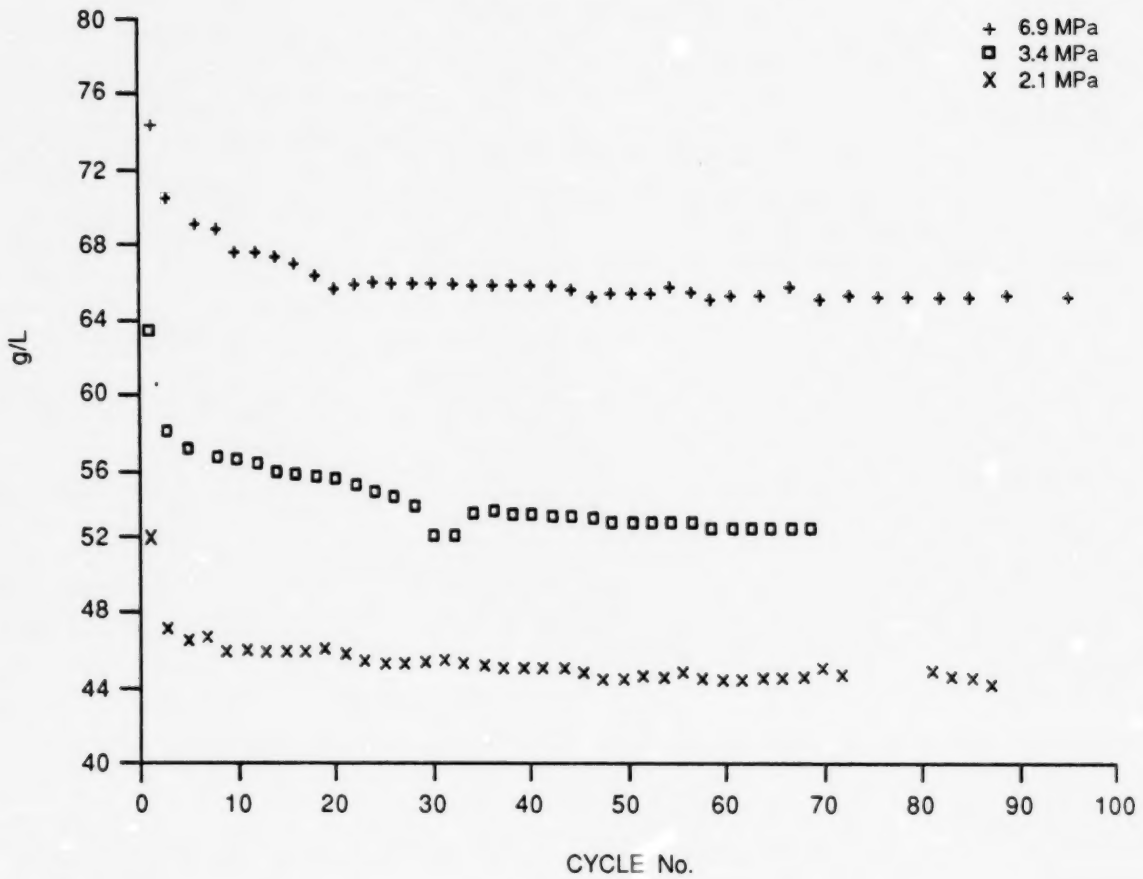


Figure 29/ Cycling Test - Saran Carbon, Amount Delivered after 15 min Fill

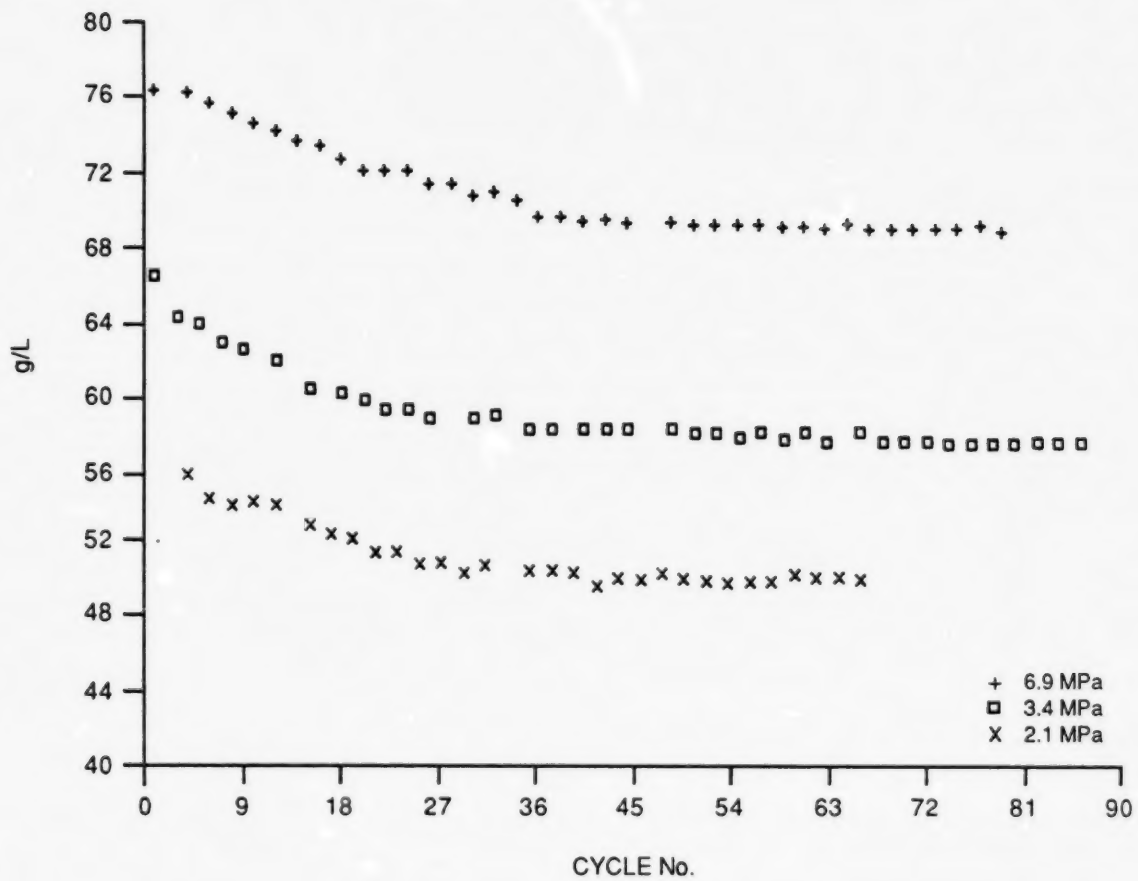


Figure 30/ Cycling Test - Saran Carbon, Amount Delivered after 4 h Fill

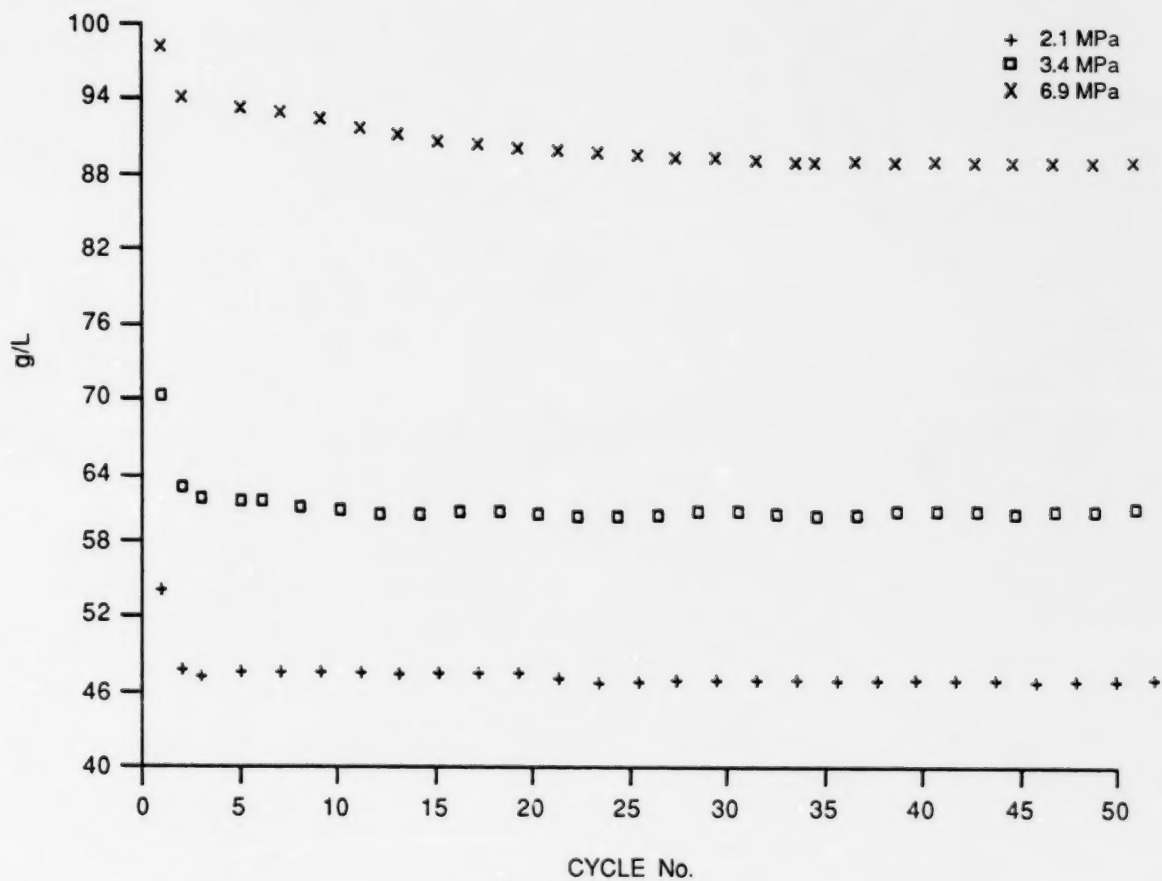


Figure 31/ Cycling Test - 50/50 AX-21/Saran Carbon, Amount Delivered after 15 min Fill

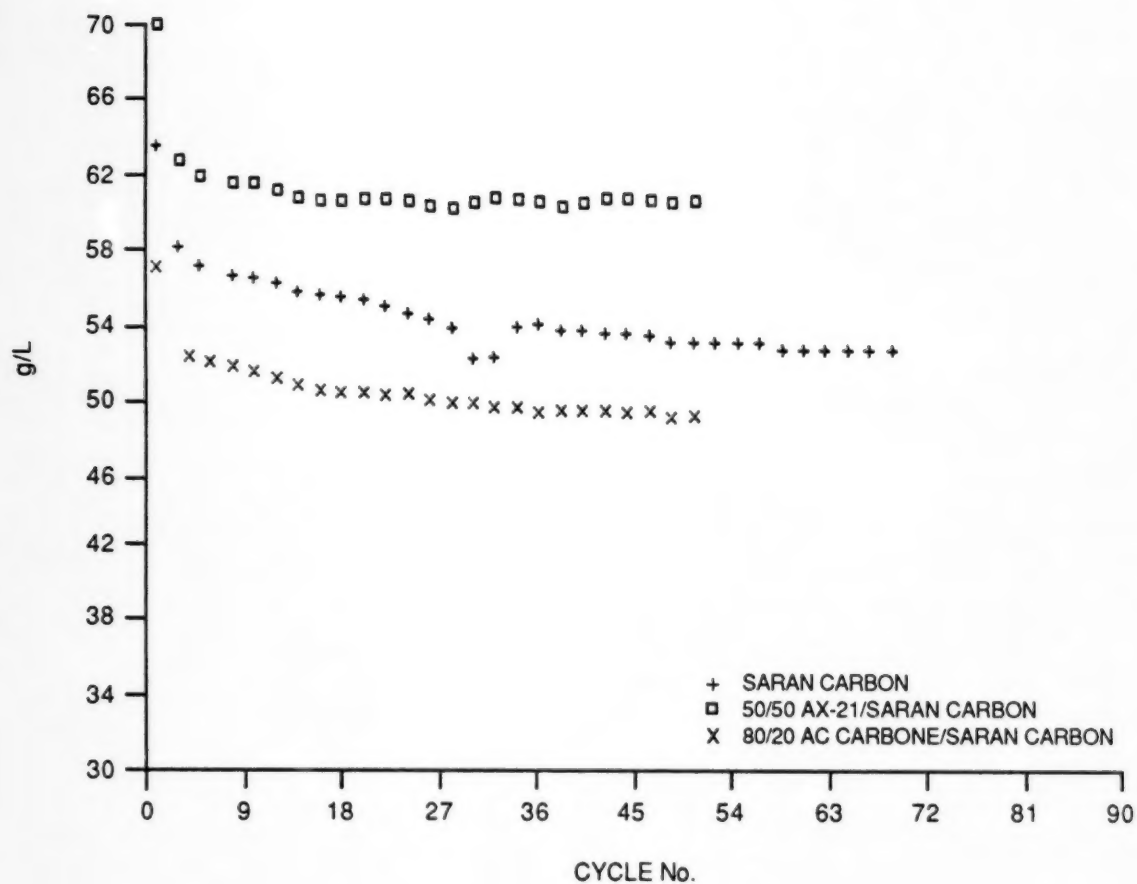


Figure 32/ Cycling Test – Amount Delivered for 3.4 MPa (500 psi) and 15 min Fill

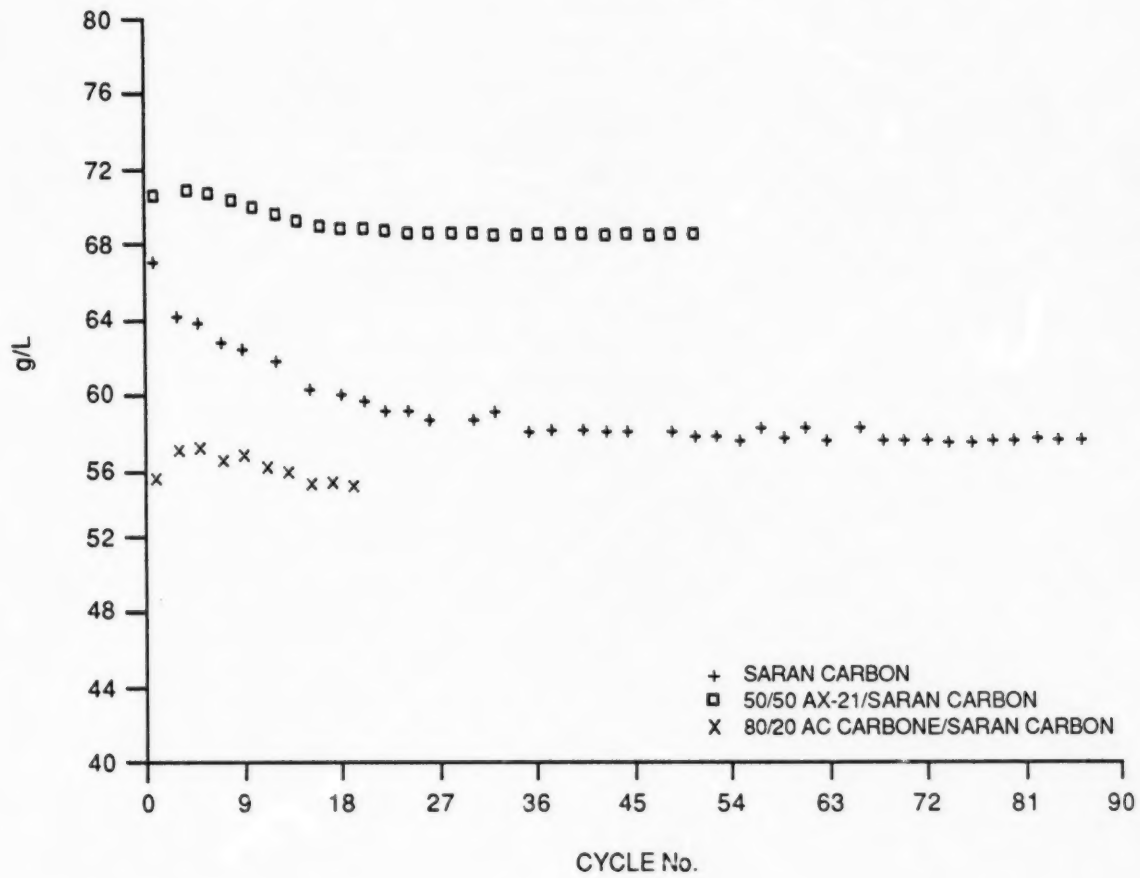


Figure 33/ Cycling Test – Amount Delivered for 3.4 MPa (500 psi) and 4 h Fill